UNIV.OF
TORONTO
LIBRARY

Presented to
The Library
of the
University of Toronto
by
Professor E. W. McHenry

Digitized by the Internet Archive
in 2010 with funding from
University of Toronto

http://www.archive.org/details/p2iecindustriale13amer

Chem & Phys
I

The Journal of INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society
Vol. 13, ~~No. 7~~ JULY, 1921 $7.50 per Year

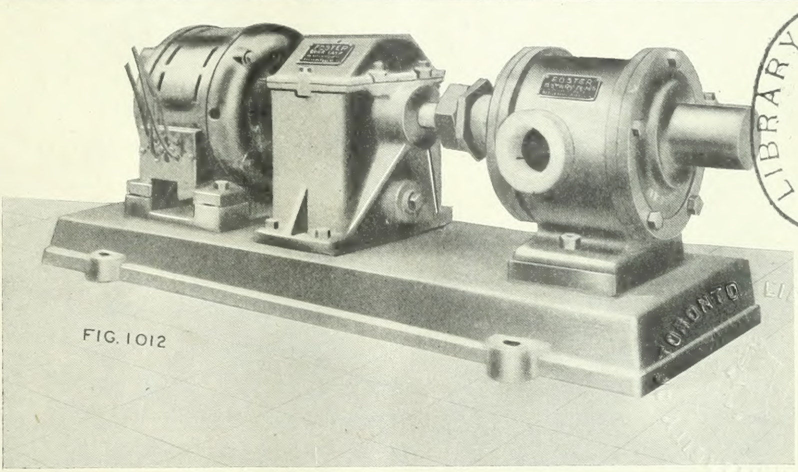


FIG. 1012

Foster Motor Driven Rotary Pump.

FOSTER ROTARY PUMPS are noted for their high suction lifts, positive pressure, and uniform flow. For handling large volumes against medium heads they are unsurpassed.

They will handle with satisfaction liquids and substances that can be moved thru pipe lines.

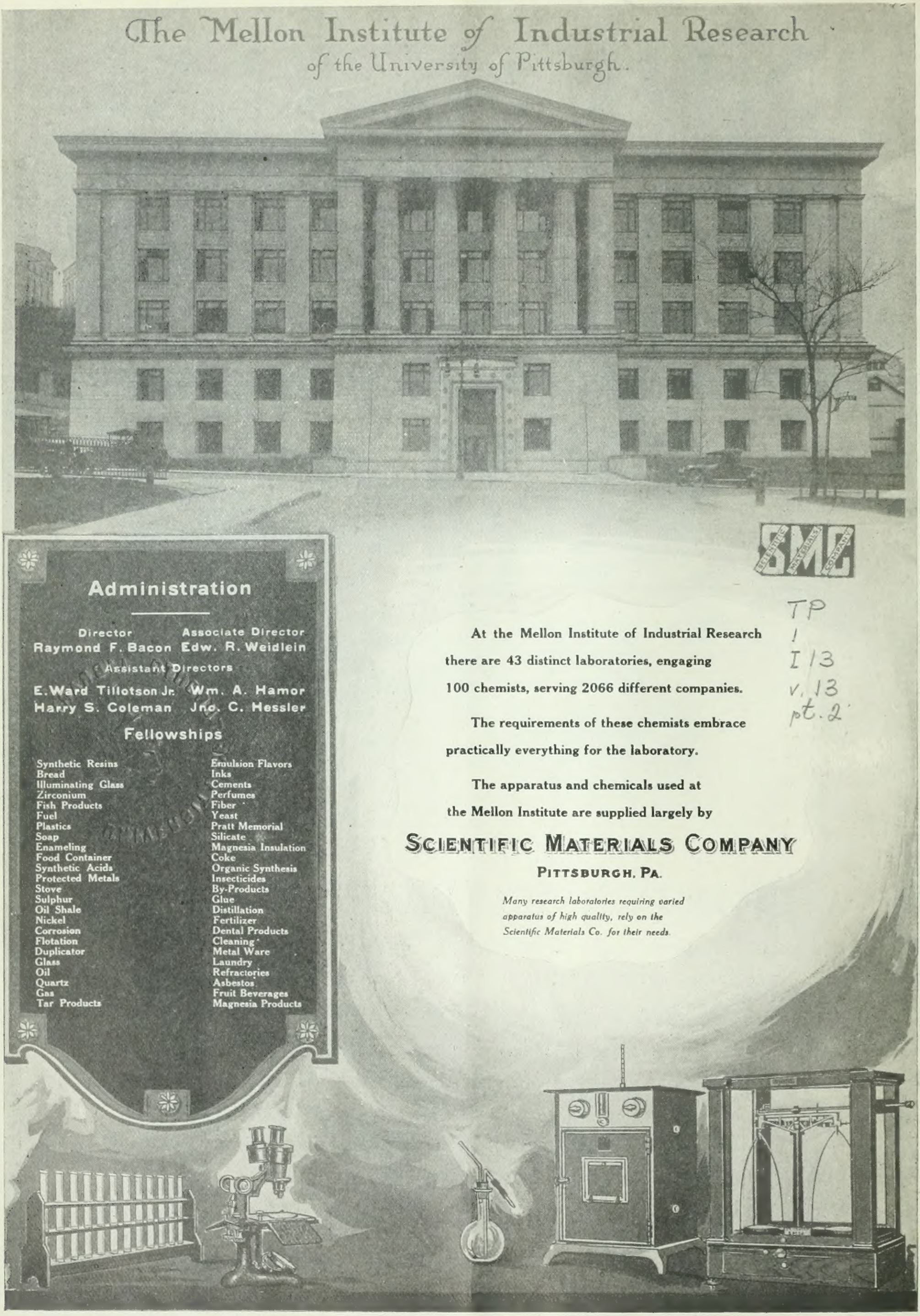
We also manufacture Steam Pumps, Well Pumps, Power Pumps, and Air Compressors.

Send for Bulletins.

FOSTER PUMP WORKS, INC.
46 Bridge St. Brooklyn, N. Y.

LIBRARY SEP 27 1934 UNIVERSITY OF TORONTO

306989
4.12.34



The Mellon Institute of Industrial Research
of the University of Pittsburgh.

Administration

Director
Raymond F. Bacon

Associate Director
Edw. R. Weidlein

Assistant Directors
E. Ward Tillotson Jr.
Wm. A. Hamor
Harry S. Coleman
Jno. C. Hessler

Fellowships

Synthetic Resins
Bread
Illuminating Glass
Zirconium
Fish Products
Fuel
Plastics
Soap
Enameling
Food Container
Synthetic Acids
Protected Metals
Stove
Sulphur
Oil Shale
Nickel
Corrosion
Flotation
Duplicator
Glass
Oil
Quartz
Gas
Tar Products
Emulsion Flavors
Inks
Cements
Perfumes
Fiber
Yeast
Pratt Memorial
Silicate
Magnesia Insulation
Coke
Organic Synthesis
Insecticides
By-Products
Glue
Distillation
Fertilizer
Dental Products
Cleaning
Metal Ware
Laundry
Refractories
Asbestos
Fruit Beverages
Magnesia Products

SMC
SCIENTIFIC MATERIALS COMPANY

At the Mellon Institute of Industrial Research there are 43 distinct laboratories, engaging 100 chemists, serving 2066 different companies.

The requirements of these chemists embrace practically everything for the laboratory.

The apparatus and chemicals used at the Mellon Institute are supplied largely by

SCIENTIFIC MATERIALS COMPANY
PITTSBURGH, PA.

Many research laboratories requiring varied apparatus of high quality, rely on the Scientific Materials Co. for their needs.

TP
1
I13
v.13
pt.2

The Journal of
INDUSTRIAL & ENGINEERING CHEMISTRY
Published Monthly by The American Chemical Society

Editor: CHAS. H. HERTY
Assistant Editor: LOIS W. WOODFORD
Advisory Board: H. E. BARNARD, J. W. BECKMAN, A. D. LITTLE, A. V. H. MORY, CHAS. L. REESE, GEO. D. ROSENGARTEN, T. B. WAGNER

EDITORIAL OFFICES:
One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613–0614

Cable Address: JIECHEM

ADVERTISING DEPARTMENT:
170 Metropolitan Tower
New York City
TELEPHONE: Gramercy 2145

Volume 13 JULY 1, 1921 No. 7

CONTENTS

EDITORIALS:

Fair Weather Predictions ... 590
Facts Supplant General Statements ... 590
The Chemist and the Railways ... 591
Alcoholic Tribulations ... 591
Congressional Recognition of Chemistry ... 592

THE CHEMICAL INDUSTRY AND TRADE OF HOLLAND. O. P. Hopkins ... 593

ORIGINAL PAPERS:

Vacuum Drying. Charles O. Lavett and D. J. Van Marle ... 600
Potash from Kelp. IV—Continuous Countercurrent Lixiviation of Charred Kelp. J. W. Turrentine and Paul S. Shoaff ... 605
A Study of the Fundamental Laws of Filtration Using Plant-Scale Equipment. Fred P. Baker ... 610
The Thermal Decomposition of Shales. I.—Heat Effects. Ralph H. McKee and E. E. Lyder ... 613
Studies on the Toxicity of Wood Preservatives—III. C. J. Humphrey, Ruth M. Fleming and E. Bateman ... 618
The Toxicity of Various Fractions and Combinations of Fractions of Coal-Tar Creosote to Wood-Destroying Fungi. Henry Schmitz and Sanford M. Zeller ... 621
Nitrocellulose and Its Solutions as Applied to the Manufacture of Artificial Leather. W. K. Tucker ... 623
An Experimental Study of the Significance of "Lignin" Color Reactions. Ernest C. Crocker ... 625
The Calcium Chloride Method for the Determination of Water in Gasoline and in Certain Other Substances. Charles W. Clifford ... 628
The Solubility of Water in Gasoline and in Certain Other Organic Liquids, Determined by the Calcium Chloride Method. Charles W. Clifford ... 631
Determination of the Volatile Matter in Graphite. Owen L. Shinn ... 633
Discoloration in Canned Sweet Potatoes. Edward F. Kohman ... 634
Composition of Hollyhock Seed and Oil. R. S. Hiltner and L. Feldstein ... 635

LABORATORY AND PLANT:

A Modification of the Dumas Method, and the Application of the Kjeldahl Method to the Determination of Nitrogen in Nitronaphthalenes. Paul H. M.-P. Brinton, F. M. Schertz, W. G. Crockett and P. P. Merkel ... 636
Uniform High Temperature throughout a Large Volume. E. F. Northrup ... 639
A Rotary Digester for Use in Bagasse Analysis. Guilford L. Spencer ... 640
Continuous Sampling of Sugar Liquors. Walter L. Jordan ... 640

ADDRESSES AND CONTRIBUTED ARTICLES:

Incendiaries in Modern Warfare. Arthur B. Ray ... 641
Industrial Alcohol and Its Relation to Prohibition Enforcement from the Manufacturer's Standpoint. M. C. Whitaker ... 647

SOCIAL INDUSTRIAL RELATIONS:

The Biological Trend of Industry. H. W. Jordan ... 650
Spare Time ... 651

SCIENTIFIC SOCIETIES:

Local Sections Protest against Industrial Alcohol Restrictions; Detroit Meeting of the American Institute of Chemical Engineers; National Lime Association Holds Annual Convention; Seventh National Exposition of Chemical Industries; Calendar of Meetings ... 651

NOTES AND CORRESPONDENCE:

Coöperative Analytical Work of the American Oil Chemists' Society; The Volumetric Determination of Aluminium in Its Salts—Correction ... 655

MISCELLANEOUS:

National Research Council ... 609
Monthly Statistical Service on Production and Stocks of Sulfuric Acid and Nitric Acid ... 624
Insecticide and Disinfectant Manufacturers Association ... 624
Honors to Sir John Harrison ... 632
A. C. S. Monograph on "Glue and Gelatin" ... 632
A Grant for Research ... 632
Assignment of Patents ... 646
Civil Service Examinations ... 655
Utilization of Niter Cake ... 655

WASHINGTON LETTER ... 656
PARIS LETTER ... 657
INDUSTRIAL NOTES ... 658
PERSONAL NOTES ... 658
GOVERNMENT PUBLICATIONS ... 659
BOOK REVIEWS ... 662
NEW PUBLICATIONS ... 666
MARKET REPORT ... 667

Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted.
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.

EDITORIALS

Fair Weather Predictions

One fixed determination in the office of THIS JOURNAL has been that the monthly issue shall always be ready to go into the mails on the appointed date. The staff has loyally coöperated in this effort, regardless of hours of work. With the notice given in April of an impending strike on the first of May, the matter passed beyond our hands, and when the strike materialized, the record of promptness was effectually shattered.

Fortunately for our peace of mind, the Council of the SOCIETY, representative of the membership, had agreed, by formal resolutions adopted at the Rochester Meeting, to wait indefinitely for journals, thereby materially assisting the printer in his stand against what he considered unjust demands from the striking employees.

The labor conditions affected most seriously the hand composition work in the printing office, and this force has been recruited on an open shop basis until it is now greater in number than before. Naturally, men not accustomed to printing chemical articles have had to be developed and trained, so that the new force, at first quite inefficient, is gaining steadily in efficiency. There is now every prospect that the August issue will quickly follow and that the September issue will go into the mails promptly on the last day of August. Pardon anachronisms in the editorials of the July and August issues, in view of the unusual situation.

With all of these troubles upon us, there has been one pleasurable aspect of the situation, the hearty coöperation of both authors and advertisers in the effort to get our work upon a right and permanent basis. Letters received, especially from advertisers, make us feel that there is a strong bond between THIS JOURNAL and its patrons, and we desire here to express our sincere appreciation of that spirit.

One further word only to the authors of papers is added. The preparation of reprints requires a considerable amount of hand composition work and remaking of material. We urge authors to be extra patient in the matter of receiving their reprints. If the present composition force is diverted to work on reprints, the issue of each of the journals of the SOCIETY would be delayed to that extent. We have, therefore, taken the liberty of authorizing the printer to postpone the making up of reprints from THIS JOURNAL, and to put all emphasis upon catching up with the regular schedule of publication. We are confident of an extension of loyal coöperation on the part of our contributors.

To adopt the language of the Weather Bureau: "For to-morrow: fair weather."

Facts Supplant General Statements

In a former editorial entitled "Thinking It Through" (THIS JOURNAL, March 1921, p. 186), there was pointed out the present world over-productive capacity for dyes, resulting from the large war-time increases in the capacity of German dye plants and from the establishment of dye industries amply sufficient for domestic needs in countries which before the war had absorbed a greater part of the output of the German plants. These countries have been led to this step by a clear recognition of the tremendous bearing of the dye industry upon war preparedness because of developments in chemical warfare.

It was further pointed out that the continued existence of these great German plants constituted a distinct threat against the peace of the world in the most modern form of warfare, and it was urged that when the question of disarmament should be taken up between the nations, chemical disarmament should receive serious and earnest consideration.

Upon the invitation of this country there will be assembled in Washington within the next few months a representative gathering of the ablest minds from five of the leading nations of the world to discuss not only questions of naval disarmament but to consider on broad lines questions connected with future peace.

On July 16, 1921, Congressman Longworth read to the House of Representatives (*Congressional Record*, 67th Congress, page 4086), the following letter from General John J. Pershing:

> GENERAL OF THE ARMIES
>
> Washington, July 15, 1921
>
> Hon. Nicholas Longworth,
> House of Representatives, Washington, D. C.
>
> Dear Mr. Longworth: With reference to the protection for the dye industry in this country, it can be stated that the coal-tar products, of which dyes are the most important at present in peace, is the base of practically all of our high explosives and most of our war gases.
>
> Our shortage of chemical plants in general, and dye plants in particular, prior to the World War, made it difficult for us to obtain a supply of high explosives and gases until we had been in the war for several months.
>
> From the above the importance of the chemical industry from a military standpoint will be readily seen.
>
> Sincerely yours,
> (Signed) JOHN J. PERSHING

This letter is of deepest significance as bearing upon the question of disarmament.

In substantiation of our contention of the potential disaster which may await the world from the German dye plants, we have been furnished by a former military officer closely connected with all of the chemical warfare activities of the allied and associated powers in the recent war, figures which give a vivid impression of the tremendous capacity of those plants.

Under the Versailles Treaty of Peace, Article 16, Title III, the stock of ammunition allowed Germany is as follows:

CALIBER	NO. OF ROUNDS
7.7-cm. gun	204,000
10.5-cm. howitzer	67,200
Light trench mortar	151,200
Medium trench mortar	25,200

From official records of German shell, the capacity of shell filling is given in the following table:

CALIBER	BURSTING CHARGE KG.	TOTAL EXPLOSIVES REQUIRED, TONS
7.7-cm. guns	0.93	189.72
10.5-cm. howitzers	2.00	134.40
Light trench mortar	0.50	75.60
Medium trench mortar	10.00	252.00
Total		651.72

The use and manufacture of poison gas in Germany is entirely forbidden by the Treaty; therefore no stock allowed should be gas-filled. But, as the cartel could produce gas for shell filling, we must, in providing for future disarmament or war, include gas filling as a matter to be dealt with. The Treaty stocks, therefore, appear as follows:

CALIBER	GAS CONTENT LITERS	TOTAL GAS REQUIRED LITERS	TOTAL GAS REQUIRED TONS
7.7-cm. shell	0.850	173,400	253.164
10.5-cm. howitzer	1.285	86,352	126.074
7.6-cm. trench mortar	0.500	75,600	110.376
Medium trench mortar	8.000	201,600	294.336
Total		536,952	783.950

In the end column, the weight of gas is calculated by means of assuming an average density for the gas, in this case 1.46.

The average weekly war production of explosives by the cartel was 2376 metric tons; the average weekly production of gas, 817 tons. In one week the cartel could produce 3.64 times more explosives and 1.04 times more gas than that required to fill the Treaty stocks. Using both types of shell, the cartel would cover the task in less than two days (1.6 days).

While we are endeavoring to decrease the possibility of war and certainly to diminish the burden of taxation by a limitation of naval armament, surely the task will be incomplete if we ignore the existence to-day of such terrific gas-producing power as now exists in Germany. To those who would endeavor to minimize this danger by designating such discussion as hysterical, we would again say "Think it through."

The Chemist and the Railways

It was our good fortune and pleasure recently to address the annual meeting of the American Railway Development Association. It was a live bunch, men who are constantly on the lookout for means of furthering the development of the territory traversed by their several roads. It was evident from the attitude of the members that they were "sold" on the subject of chemistry as a powerful aid in industrial development. The following resolutions, passed on the final day of the meeting, confirm that impression:

Resolved: 1. That this Association recognizes the importance of chemistry in the development of agriculture and industries, and believing that it can be made an important factor in the work of its members, recommends investigation along such lines.

2. That this Association go on record as favoring coöperation between the AMERICAN CHEMICAL SOCIETY and the American Railway Development Association.

3. That the officers of this Association are requested to confer with the officers of the AMERICAN CHEMICAL SOCIETY for the purpose of bringing about such coöperation.

Alcoholic Tribulations

When the supplemental bill for the enforcement of prohibition, H. R. 5033, was first presented to Congress by Mr. Volstead, it attracted but little attention among chemists, for it was well known that the machinery for enforcement of prohibition had fallen down. This was on its face an anti-beer bill, drawn ostensibly to offset the decision of the Attorney General regarding the prescription of beer by physicians. Those of the chemical profession most closely in touch with the alcohol situation soon found that this apparently innocent bill stepped completely over the line of prohibition enforcement into the field of the distribution and utilization of alcohol for industrial purposes.

The committee appointed by the AMERICAN CHEMICAL SOCIETY at its Rochester Meeting immediately set to work to present the views of the manufacturers and users of industrial alcohol, but the efforts of the committee in the hearing before the Judiciary Committee, of which Mr. Volstead is chairman, were practically fruitless. The scant courtesy tendered the representatives of legitimate industries was amazing in view of the fact that their only plea was that the original intent of Congress as embodied in the National Prohibition Act should be carried out. It was apparent that it was expected to railroad the bill through a Congress known to be committed strongly to prohibition enforcement.

What could be done to make clear the sinister purpose of the bill in its application to the use of alcohol in the industries? Protest meetings were hastily called of the local sections of the AMERICAN CHEMICAL SOCIETY in New York, Philadelphia, and Baltimore, at which the views of chemists were put forward in no uncertain language. It was not enough, however, that the chemists should talk among themselves; their views should speedily be brought before the public at large. The A. C. S. News Service served this purpose admirably. Bulletins were sent to the press throughout the country giving extracts of speeches made and of the action taken. A flood of clippings received since the date of issuance shows how widely the chemists' point of view was given to the nation. The value of such an organization as is represented by the AMERICAN CHEMICAL SOCIETY and the wisdom of the Directors of the SOCIETY in developing by modest appropriations a genuine news service was amply demonstrated in this critical legislative situation.

Meanwhile the fight shifted to the Rules Committee of the House, for the Chairman of the Judiciary Committee, the Hon. Mr. Volstead, was endeavoring to gain a special rule for immediate consideration of his slightly modified (now H. R. 6752) supplemental bill. The Rules Committee listened patiently, however, to the views of the chemists and refused the special rule requested.

In an endeavor to bring order out of chaos, Chairman Campbell of the Rules Committee of the House, and Senator Willis introduced in the House and Senate, respectively, separate bills which embodied the strictly anti-beer sections of the supplemental Volstead bill. The Rules Committee of the House gave permission for prompt consideration of the Campbell bill. Then the foxy work began. The Chairman of the Judiciary Committee, Mr. Volstead, asked that the new bill be referred back to his committee, and there a number of most objectionable amendments were placed upon it. This modified bill was brought before the House under the rules granted for the strictly anti-beer bill and hurriedly passed. By the press it was hailed as simply an anti-beer bill, but a reading of the bill showed plainly the tricky character of the legislation. Again representations were made by the committee of chemists to the Judiciary Committee of the Senate, now in charge of the bill. A number of the objectionable items were stricken out by the Senate committee, but it was reported with several unfortunate features retained. As it stands on the Senate calendar, at a time when all are decrying autocratic powers by government officials, it puts in the hands of the Prohibition Commissioner the absolute power to wreck many legitimate industries if in his zeal for prohibition enforcement he overlooks the rights of industries many generations old because existing regulations may have been abused by a few topers. Debate on the bill (H. R. 7294) is now in progress in the Senate. The character of the debate, however, is largely confined to constitutional questions involved and to a defense of the right of the physician to prescribe what he desires for his patient.

Meanwhile no evidence can be found of any disposition to carry out the feature of the existing law which declares for the encouragement of the production of alcohol and its use in the legitimate industries of the country, despite the many protests which have been registered by the chemical industries and the AMERICAN CHEMICAL SOCIETY. Far from this, it requires no expert eye to note the inefficiency in many stages of manufacture of alcohol for industrial purposes which result from government regulations in such plants, all of which adds necessarily to the cost of production of alcohol and therefore decreases the ability of our industries using this important reagent to compete with similar industries in lands where no such restrictions prevail.

The present-day taxation of alcohol is a striking paradox. For many years taxation of alcoholic beverages proved an important source of government revenue. Theoretically such beverages do not exist to-day. Yet the tax upon alcohol for many purely industrial purposes continues. As the chemist looks down upon the row of reagent bottles upon his shelf, he finds no other reagent which he utilizes in his work subject to such a tax. It is a peculiar hang-over of pre-prohibition days and a striking testimonial of the failure of government bureaus to provide such machinery as will encourage the use of alcohol for industrial purposes without leaving the door open for misuse. The tax on alcohol in prohibition times is just as illogical as was the proposal during the drafting of the Revenue Act to put a tax upon moonshine stills.

Congressional Recognition of Chemistry

Believing as we do in the representative character of the Congress of the United States, it has been a matter of intense interest to await the outcome of the work of the Ways and Means Committee of the House of Representatives on the formulation of the tariff bill. This interest has been due to a desire to see demonstrated how far the American people have been aroused to a conception of the chemical industries as a national asset in both peace and war.

A cursory reading of the bill just submitted shows plainly that this thought has been thoroughly and sympathetically grasped by our representatives, for, taken as a whole, Schedule 1 (formerly Schedule A) of Tariff Bill H. R. 7456 must carry to every one interested in chemistry a feeling of hope and encouragement. Should it become law, there can be no doubt of busy times ahead, for it will encourage capital to invest in the chemical industries and will inspire chemists to go about their work with a spirit of confidence, determination, and responsibility to the nation.

The task of drafting Schedule 1 has been a complex one ably carried out by the subcommittee, consisting of Congressmen Longworth of Ohio, Copley of Illinois, and Hadley of Washington. In this intricate field, it is evident that they have been splendidly aided by the thorough studies of the chemical industry carried out during the past three years by the U. S. Tariff Commission.

The coal-tar chemical section has been drawn along the lines pointed out by Mr. Longworth in his address before the AMERICAN CHEMICAL SOCIETY at its Rochester Meeting this spring. A bitter fight has been made upon this section by the importers and by a small group who believe in tariff even at the sacrifice of protection.

Firm support has been given to the American potash industry in the form of a five-year sliding scale ad valorem tariff. This was the minimum tariff on which the potash producers claimed the industry could be developed in this country. If this section is adopted, the responsibility will rest upon those engaged in this industry to make this country economically independent of foreign potash.

Space does not admit detailed discussion of the many features involved in Schedule 1, but for the benefit of those who consult the bill and find therein no mention of protection for the products they manufacture, attention is called to the basket clause, paragraph 5 of Schedule 1, page 3 of the bill:

> "All chemical elements and all chemical and medicinal compounds, preparations, mixtures and salts, and combinations thereof, all the foregoing obtained naturally or artificially and not specially provided for, 25 per centum ad valorem."

The whole question of depreciated foreign exchange is taken out of the mire by the incorporation in the bill of an American valuation clause for assessment of ad valorem duties. This wise provision of the bill eliminates gross inequalities under the present conditions of foreign exchange and places all importations from whatsoever country on absolutely the same basis.

To Chairman Fordney and the members of his committee sincere appreciation of their sympathetic support of the chemical industry is due. Especially careful have they been in making provisions for the continuation of those industries which sprung into existence because of war needs. They have left no doubt of their conviction on that subject. The bearing of the dye industry on the question of national defense and the future of medicine is clearly set forth in the following extract from the Committee's Report:

> A nation, therefore, which has a thoroughly complete dye industry capable of supplying its dye needs is always prepared for defensive or offensive war so far as the production of explosives and chemical gases is concerned, and the experiences of the late war have proved that without these chemical essentials any nation under modern conditions is impotent either in attack or defense.
>
> If, therefore, as seems likely, we are entering upon a period of international disarmament, possession of such an industry becomes of infinite importance. During such a period a nation possessing such a potential arsenal would be in a position to overwhelm any nation less well endowed and would be practically immune from attack.
>
> Of perhaps equal importance from another point of view in the case of this industry is its bearing upon the advancement of medical and industrial chemistry. It is the one industry which deals on a gigantic scale with organic chemistry, and it is upon organic chemistry that progress of modern medicine rests. Salvarsan, for instance, was developed in a dye works laboratory and is the first known certain cure for one of the most terrible scourges of humanity. Scientists confidently predict that upon further development of organic chemistry will rest the discovery of cures for tuberculosis and other devastating diseases, even such as cancer. This development must rest upon a further development in this country of skilled chemists, and it is only in a dye laboratory that large numbers of such chemists can find a livelihood.
>
> A well-developed dye industry here will furnish a great reservoir of technically trained men and of scientific knowledge upon which the most important industries of the country may draw in time of peace and the Nation itself in time of wai or threatened war.
>
> The present dye industry in this country is absolutely a product of the late war. Up to that time Germany controlled the market of the world in dyestuffs, and such dye works as we had here were mere assembling plants for German materials and supplied only about one-tenth of the American market. To-day more than 200 different concerns are supplying something like 90 per cent of the American market for coal-tar products in quantity, though not in value. The absolute necessity of saving and fostering such an industry as this would seem to be beyond argument, and the only question that should arise is by what legislative method can its permanent continuance be assured?
>
> Your committee is of the opinion that no tariff duties, no matter how high, can meet the conditions that would arise when Germany is again in a position to force her dyes and dyestuffs upon the American market. However other German industries may have suffered as a result of the war, the German dye syndicate is as rich and powerful as ever. The great dye factories during the war were turned over to the production of explosives and poison gases and the chemists and laborers in these factories were immune from the draft. A vast amount of dyes and dyestuffs has been accumulated in recent years and their factories are now running at full time in the production of others, and the whole huge German dye industry, capable before the war of supplying the entire demand of the world, is now combined in a single immense trust organized on purpose to fight its way back to the former German world monopoly.
>
> Utterly unscrupulous as the German syndicate was before the war when its supremacy was uncontested, practicing ruthlessly every form of corrupt and unfair competition known to commerce, it is inevitable that in the almost immediate future, when instead of safe supremacy it faces possible destruction, it will attack all competitors with reckless disregard of business decency.
>
> That attack inevitably will be concentrated upon us. France and Japan some time ago in the interest of their Government-aided dye industries placed more or less complete embargoes upon the importation of dyestuffs. Only recently Great Britain and Italy have placed a complete embargo upon dyestuffs—in the case of Great Britain for a period of 10 years. Russia is out of business. The market of the United States, therefore, is, except that of China, Germany's last opening. To penetrate it and destroy our domestic industry she will stop at nothing.
>
> Under such conditions your committee is of the opinion that nothing short of a limited embargo will enable the American industry to continue in existence.

Will the House in its final vote on the bill support the proposals of its Committee on Ways and Means?

THE CHEMICAL INDUSTRY AND TRADE OF HOLLAND

By **O. P. Hopkins**
1824 Belmont Road, Washington, D. C.

Without native supplies of the raw materials essential to manufacturing industries, Holland is primarily an agricultural and commercial nation, making the most of a soil and topography well suited to grazing and cereal and potato production, and of excellent river and harbor facilities for shipping. Such manufacturing industries as exist are based almost entirely upon imported materials, of which a considerable portion comes from the rich Dutch colonies. Part of the importing, however, is carried on for the purpose of reëxporting. The prosperity of the country is due quite as much to the industry, thrift, and intelligence of the people as to other factors.

Since the war the import trade has been concerned chiefly with foodstuffs, iron and steel and nonferrous metals, coal, tobacco, textiles and yarn, mineral oil, coffee, fertilizers, and oilseeds. The principal items in the export trade have been tobacco, butter and butter substitutes, textiles, skins, paper, sugar, cheese, mineral oil, coffee, iron and steel, and paints and colors.

Depending largely on water-borne commerce, Holland, as a neutral and because of her geographical location, was sorely tried by the war, although for a period after hostilities began she prospered. As time went on and the blockade of the Central Powers was strengthened, it became more and more difficult to carry on trade with her neighbors, neutral or belligerent, until finally it was something of a problem to get in sufficient quantities for purely domestic needs. Since the war there has been a revival in the trade of the country, for the Dutch traders are in an excellent position to handle a portion of the import and export business of Germany.

SUMMARY OF TRADE IN CHEMICALS

So far as the chemical trade is concerned, Holland is very closely linked to Germany. A really good market exists for imported chemicals, but the lion's share not unnaturally goes to the great chemical industries that are so conveniently located next door and that now have an immense advantage in the exchange rate. The export trade in domestic chemical products, never so important as the import trade, is handicapped at present by the high price of Dutch money.

The following figures give an approximate idea of the foreign business in chemicals for the last four years for a group in the Dutch statistics that includes chemicals, medicines, dyes, colors, perfumery, explosives, matches, glue and gelatin, ink, and celluloid:

	Imports		Exports	
Year	Metric tons	Value	Metric tons	Value
1917	59,000	$13,000,000	22,000	$9,000,000
1918	35,000	11,000,000	4,000	3,000,000
1919	97,000	19,000,000	33,000	12,000,000
1920	177,000	32,000,000	60,000	21,000,000

It is evident that the trade made a fine recovery from the almost complete stagnation of the war year, although as a matter of fact the world-wide depression that made itself felt about the middle of 1920 affected the Netherlands as it did other countries. Nevertheless, in spite of the good business of 1920, the Dutch chemical manufacturers are much concerned at the appearance of low-priced products from the old source of supply, Germany, where the exporters are not only anxious to reëstablish themselves in their former markets, but have a decisive advantage in exchange. Dutch manufacturers also claim that the prices of German chemicals have been lower than the prices of German raw materials from which the chemicals are manufactured.

The principal imports in 1920 were: Aniline dyes and indigo ($5,537,000), colors, paints, and varnishes ($4,675,000), sodas ($3,991,000), and perfumery, etc. ($1,899,000). The leading exports were: Colors, paints, and dyes ($7,503,000), glues and gelatin ($1,688,000), perfumery, etc. ($1,668,000), and quinine salts ($1,338,000).

DOMESTIC CHEMICAL INDUSTRIES

The chief Dutch industries that may be classed as chemical are those concerned with the manufacture of vegetable oils, paints, varnishes and colors, superphosphates, soap, and quinine salts, all of which work on raw materials imported from foreign countries or from the colonies. There are no figures available to show production since the war, but some census statistics for 1913 and the latest available year are given below to afford an idea of the relative standing of the industries. Fertilizers are not included. In some cases returns were not asked for or not made, and where figures are not given it must not, therefore, be assumed that there was no production. The grouping is that adopted in the original census.

	1913	1916
HYDROCHLORIC AND SULFURIC ACIDS		
Sulfuric acid (60°–66° Bé.)	$181,703	$604,272
Hydrochloric acid	.....	51,804
Other products	36,298	40,309
TOTAL	218,001	696,385
PHARMACEUTICAL CHEMICALS		
Quinine and allied alkaloids and their salts	.....	3,121,327
Other alkaloids	....	157,965
Spring salts, artificial	..	6,118
Medicinal wines	..	35,713
Sirups	..	11,738
Disinfectants	...	5,050
Other products	....	835,161
TOTAL	....	4,173,072
ASPHALT WORKS AND COAL-TAR DISTILLERIES:		
Benzene	14,929	....
Disinfectants	.....	63,198
Carbolineum	.....	50,436
Oils (anthracene, creosote, and other)	124,401	182,420
Other products of distillation	60,833	117,659
Cement mastic	143,860	166,062
Mastic, pitch, black varnish	154,860	229,529
Asphalted paper	217,449	355,103
TOTAL	716,332	1,164,407
PIGMENTS AND DYES:		
Blue dyes and pigments	79,163	294,261
Coal-tar dyes	86,148	235,574
Other dyes and pigments	68,155	147,892
White lead, zinc white, and lithopone	2,061,116	4,325,908
Other products	23,290	104,048
TOTAL	2,317,872	5,107,683
PREPARED COLORS, LAKES, AND VARNISHES		
Varnishes	1,035,170	1,089,209
Lakes	1,298,189	1,327,000
Prepared colors	675,770	1,220,266
Water colors	27,182	55,502
Dry colors	15,068	218,930
Oil	334,107	324,840
Other products	64,910	210,743
TOTAL	3,460,396	4,446,490
BLUING		
Bluing	23,535	45,619
Other products	12,748	52,381
TOTAL	36,283	98,000
INKS AND BUREAU ARTICLES		
Writing ink	.	74,883
Printer's ink	.	184,206
Glue, liquid		7,224
Sealing wax	.	39,651
Library paste	.	6,923
Other products	.	85,071
TOTAL	.....	397,958

	1913	1916
GLUE AND SIZE:		
Glue and sizing	46,364	71,823
Other products	25,675	46,282
TOTAL	72,039	118,105
OIL MILLS:		
Linseed oil (including boiled)	5,202,617	10,208,043
Rapeseed and colza oils	1,263,625	2,044,547
Sesame oil	....	4,880,352
Peanut oil	.	64,112
Soy-bean oil	166,950	241,380
Coconut oil	. ..	12,286,037
Palm-kernel oil	. .	3,156,107
Other oils and fats	2,139,518	1,927,877
TOTAL OILS	8,772,710	34,808,455
Oilcakes	8,556,541	18,175,000
Other products	804,639	2,017,636
Work done for others	6,720	1,201,255
TOTAL PRODUCTION	18,140,610	56,202,346
MACHINE OIL:		
Machine and other oils	13,427	109,769
Other products	.....	56,788
TOTAL	13,427	166,557
		1915
SOAP:		
Soft soap	1,559,844	3,447,577
Soft textile soap	3,988	34,895
Hard soap	739,313	1,671,151
Liquid and medicated soap	7,813	12,506
Soap powder	794,367	1,440,411
Eau de Cologne and perfumery	345,353	348,108
Glycerol, raw and refined	288,538	573,420
Linoleic acid	196,613	351,096
Other fatty acids	102,877	252,226
Other products	162,726	340,509
TOTAL	4,201,432	8,471,899
		1916
BLACKING AND POLISHES:		
Polishes	43,697	106,437
Shoe blacking	75,444	324,243
Various waxes	45,724	71,562
Axle grease, leather polish, etc.	15,385	31,847
Other products	29,860	85,078
TOTAL	210,110	619,167
WAX AND CANDLES:		
Beeswax, refined	202,545	267,820
Wax and other candles	35,393	61,139
Other products	1,018	4,199
TOTAL	238,956	333,158
COMPRESSED GASES	93,039	201,454
PETROLEUM PRODUCTS	1,617,275	380,073

VEGETABLE OILS

Although there is no oil-milling center in the Netherlands to rival Hull, Marseille, and Hamburg, the crushing of oil-bearing materials is nevertheless an extensive industry, playing an important part in the economic life of the country. Vegetable oil is an essential in the manufacture of margarine, which is produced in great quantities to supplement the output of dairy butter. Linseed oil is in great demand by the thriving paint and varnish industry, and oilcake finds a ready market in a country noted for its dairy industry.

With the exception of some linseed and rapeseed, all the oil-bearing materials are imported. The pre-war purchases of oilseeds totaled about $40,000,000 annually, and $14,000,000 worth of oils were also imported. Owing to shipping facilities, considerable quantities of both seeds and oils were imported for distribution to nearby markets, the exports of seeds amounting to $23,000,000 in 1913 and of oils to $8,000,000. The United States has never been prominent in the trade except as a source of cottonseed oil, and, since the war, as a secondary source of soy-bean oil. Corn oil is practically unknown.

The trade was badly disorganized during the war, and in 1918 was practically at a standstill. The Allies were alert to prevent supplies of the valuable food oils reaching the enemy through neutrals, and Holland found it expedient to make arrangements through the N. O. T. (Netherlands Overseas Trust) that amounted to an oil rationing. In fact, oils became so scarce that the government finally forbade the use of edible oils for technical purposes.

There was naturally a change in the character of material handled by the mills, although production figures are available only for the first years of the war, when the output was temporarily greatly increased. The production of the mills in 1913 was 153,000,000 lbs. of oils, of which 105,000,000 lbs. were linseed and 20,000,000 lbs. rapeseed. In 1916 the output had reached 357,000,000 lbs., of which 121,000,000 lbs. were coconut oil, 54,000,000 lbs. sesame, 42,000,000 lbs. palm-kernel, and only 14,000,000 lbs. rapeseed.

In 1919 the imports of seeds and oils increased enormously over the previous war year, but there was some falling off in 1920. Exports, practically nonexistent in 1918, were strong in 1919, and much stronger in some cases in 1920, especially in coconut oil. Some oil formerly shipped direct to Germany is going through Dutch hands to avoid the difficulties of the exchange situation and dealing in an enemy country (according to a consular report from Rotterdam). It is also said that Dutch oil and fat concerns have acquired interest in German margarine and other fat-working establishments.

PAINTS, PIGMENTS, AND COLORS

Dutch paints and pigments have a reputation that is worldwide, and are produced largely in excess of the domestic demand. The production of white lead, zinc white, and lithopone in 1913 was over 57,000,000 lbs., while 11,000,000 lbs. of prepared colors were manufactured, 7,500,000 lbs. of lakes, and 6,000,000 lbs. of varnishes.

The war interfered seriously with the industry, as most of the raw materials had to be imported, and foreign markets for the finished product were not easily accessible. Since the war, however, there has been a rapid recovery and business is apparently to continue good in contrast to the depression so general in other lines. The exports of white lead, zinc white, and lithopone alone amounted to 37,000,000 lbs. in 1920, or twice the total for 1919, and similar increases are recorded for colors and varnish. The Dutch industry is in a strong position to profit by the reconstruction that must go forward in some European districts regardless of cost, and in this way is able to keep going during the dull period in ordinary building construction.

FERTILIZERS

Essentially an agricultural and dairying country, depending to a considerable extent on land won at great cost from the sea, Holland is committed to the use of fertilizers on a large scale. Three or four times as much fertilizer is used to the acre as in the parts of the United States where fertilizers are used at all. The consumption of artificial fertilizers before the war may be estimated roughly at 600,000 metric tons, all the raw material for which was imported, except the gas-house liquor used in the manufacture of sulfate of ammonia.

The manufacture of superphosphate is carried on on a large scale, the total output in 1913 being 325,000 tons. This fertilizer is also extensively imported and exported, one of the best markets before the war being Russia. The phosphate is imported from the United States and Africa, and the material for the sulfuric acid from Spain, and, at least during the war, from Norway. There was a time when American phosphate was shipped to Holland, manufactured into superphosphate, and then shipped back again. Now both phosphate and superphosphate are shipped from this country to Holland, but that is the extent of our participation in the Dutch fertilizer trade.

Nitrates are imported from Chile and to some extent from Norway, and Thomas meal, potash, and sulfate of ammonia from Germany. Natural manures are also imported from neighboring countries.

The war brought about a shortage of fertilizers, and the soil has never since been brought up to the productivity of pre-war days. The Fertilizer Commission was organized to give guarantees that imports would be used properly, but the trade gradually came to a standstill. At the close of the war only potash fertilizers were being imported freely. Late in the war a trade in "sea manure" sprang up, the "manure" consisting of young mussels and starfish. The price went up from $7 to $90 a ton, and speculation was active. The trade disappeared quickly when peace was declared, partly as the result of the smell, which aroused public indignation.

DYESTUFFS

The domestic production of dyestuffs is insignificant and will probably continue so unless circumstances in some way make it advisable for the Germans to have plants in Holland. Even during the war there was not the incentive to build up an industry that existed in countries cut off from German sources. Practically the entire supply has come from Germany since artificial dyes displaced the natural product. In 1920 the imports amounted to 5,244,000 lbs., while the exports totaled 387,000 lbs. This latter figure includes dyes of domestic manufacture and those of German manufacture that actually passed into Dutch hands before being reëxported. It does not include dyes merely shipped from Germany through Dutch ports. There are no returns of the purely transit trade.

NOTES ON OTHER CHEMICAL INDUSTRIES

The manufacture of sulfuric acid is carried on rather extensively in connection with the superphosphate industry and to some extent independently, although, according to the Central Bureau of Statistics, the independent plants are not now able to compete with the Belgian product, which is favored by the rate of exchange. The total production in 1913 was 43,000,000 lbs. In general, the industry feels the effects of overproduction in other countries.

Imports of sodas have been stimulated by the return of peace. Purchases of soda ash reached 17,000,000 lbs. in 1920, as compared with only 375 lbs. in 1919 and no imports at all in 1918.

As great quantities of hides and skins, both domestic and imported, are handled, there is a thriving tanning industry and consequently a large market for tanning materials.

The cinchona bark from the colonies, the world's chief source of supply, is received at Amsterdam, and the manufacture of sulfate of quinine is a noted Dutch industry.

Starch is a valuable Dutch product and is one of the few Dutch chemical products based to any considerable extent upon a domestic material—potatoes.

THE IMPORT TRADE

The following table, compiled from official Dutch statistics, shows details of the import trade in chemicals and the extent to which Germany dominates this excellent market. Unfortunately it is not possible to make a worth-while comparison of the trade as it now exists with the pre-war trade, as a badly needed revision of the method of compiling the trade statistics took place during the war, the changes being so drastic as to make a comparison with previous figures very unsatisfactory. Quantities represent gross weights.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1918 Pounds	1919 Pounds	1920 Pounds
CHEMICALS:			
Acetates:			
Calcium	....	1,722,390	4,415,198
Belgium		421,945	....
United Kingdom		354,640	
United States		722,184	4,098,207
Copper		602	7,072
Lead		110,163	363,880
United States		26,164	
Acetone	....	78,491	121,842
Acids:			
Acetic	31,735	790,066	4,017,910
Germany	5,240	654,722	3,880,584
United Kingdom	....	99,925	....
United States	....	31,762	
Hydrochloric	37	2,855,541	6,328,887
Belgium	....	156,442	1,241,967
Germany	37	2,693,808	5,083,846

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1918 Pounds	1919 Pounds	1920 Pounds
CHEMICALS (*Continued*)			
Acids (*Concluded*)			
Nitric	....	316,782	804,550
Belgium	....	226,882	561,707
Germany	....	87,254	241,309
Oleic and other fatty acids	2,162,010	10,773,575	3,456,863
United Kingdom	2,161,150	7,910,564	2,082,579
United States		2,824,053	1,111,288
Stearic and palmitic	694	2,497,962	4,180,738
United Kingdom		333,042	443,303
United States		2,026,755	3,190,236
Sulfuric		21,069,042	84,800,330
Belgium		15,684,409	83,783,472
Germany		5,268,333	944,427
Alum	904,237	1,315,593	922,104
Germany	853,890	846,127	692,289
United Kingdom	50,347	446,300	217,228
Ammonia, liquid	4,804	572,313	10,337,558
Germany	4,804	553,755	10,255,336
Ammonium chloride	79,720	326,965	506,205
Germany	79,720	251,763	477,510
Calcium:			
Carbide		9,702,554	6,844,689
Germany		1,135,710	3,317,720
Norway		6,131,840	1,614,048
Sweden		2,281,486	1,513,643
Chloride	1,003,751	7,174,115	8,941,663
Belgium	133,940	105,886	2,271,206
Germany	736,772	4,388,369	2,474,144
United Kingdom		2,560,733	2,885,900
United States	31,747		576,019
Phosphate		3,142,577	5,598,187
Belgium		3,141,587	5,553,444
Chemicals, n. e. s.	38,721,229	29,064,410	57,948,000
Belgium	2,456,080	1,281,440	5,684,512
Germany	19,879,242	19,641,408	36,876,298
Sweden	6,346,200	166,830	4,391,072
United Kingdom	1,052,694	6,000,102	6,700,526
Dutch East Indies		204,831	159,548
United States	41,400	980,755	1,080,245
Chloroform	48	12,699	14,319
Cocaine	2	2,260	977
Copper sulfate		1,138,180	524,178
Germany		311,317	128,514
United Kingdom		430,195	389,918
United States		383,364	234
Ether, sulfuric	126	463	12,220
Ethers, fruit		22,908	31,567
Foods, chemical		211,890	272,432
Gases, compressed:			
Carbonic acid	806,748	2,241,819	4,764,848
Germany	806,748	2,238,460	4,736,631
Other (oxygen, hydrogen, etc.)	7,121	243,789	617,535
Germany	1,764	205,147	586,480
United States	....	231	750
Glycerol:			
Crude	92,473	25,662	1,115,457
Belgium			551,239
Refined	672	11,312	183,418
Iron sulfate	8,800	473,731	1,224,006
Germany	8,210	341,582	498,880
Magnesia	494,393	174,097	2,843,330
Germany	88,668	110,992	294,460
Greece			1,797,032
Medicines and drugs, n. e. s.	453,000	1,327,873	1,672,043
France		49,117	135,589
Germany	293,508	791,354	913,365
Switzerland	3,016	24,233	49,093
United Kingdom	60,147	196,963	348,663
United States	17,033	81,626	63,526
Methanol	838	69,496	62,930
Potassium:			
Hydroxide (caustic potash)	720,773	4,039,360	6,195,033
Belgium		164,868	1,048,613
Germany	714,600	3,401,312	4,970,500
Salts, n. e. s.	736,026	3,823,018	3,720,198
Belgium		655,655	1,920,600
Germany	436,859	1,484,732	1,413,573
United Kingdom		340,369	187,610
United States		966,337	
Quinine and its salts	284	167,787	463,910
Dutch East Indies	276	159,835	455,834
Sodium:			
Acetate	13	30,384	196,597
United States			74,274
Germany		30,384	30,084
Carbonate			
Crystals		12,856,169	9,617,995
Belgium		284,070	2,444,702
Germany		2,044,300	93,046
United Kingdom		10,413,941	6,133,822
Soda ash	12,428,900	39,536,707	60,327,580
France		552,280	11,681,467
Germany		22,867,048	17,103,100
Switzerland	142,046	146,874	4,456,367
United Kingdom	12,285,013	12,301,560	4,281,320
United States		375	17,009,966
Hydroxide (caustic soda)	5,447,428	11,794,079	19,778,624
Belgium		3,043,256	4,953,258
Germany	230,222	4,385,450	680,527
Spain			6,107,865
United Kingdom	4,899,394	3,791,170	4,109,206
United States	315,415	11,581	3,850,739
Nitrate, refined		160,847	888,368
Sulfate (Glauber salt)		8,377,986	10,939,012
Belgium		1,056,307	4,758,473
Germany		5,625,458	1,561,741

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1918 Pounds	1919 Pounds	1920 Pounds
CHEMICALS (*Concluded*):			
Sodium (*Concluded*):			
United Kingdom	..	1,696,221	3,730,681
Tetraborate (borax)	81,728	1,947,854	2,276,508
Belgium	.....	101,684	498,251
United Kingdom	81,631	1,436,186	1,518,753
United States	.....	403,349	.....
COAL-TAR PRODUCTS:			
Anthracene	...	.....	5,487
Asphalt	659,603	1,052,900	1,166,483
Germany	395,525	835,576	458,575
United Kingdom	....	210,195	535,335
Benzene	.....	555,188	289,482
United Kingdom	...	540,044	252,224
Carbolineum	24,440	374,424	60,625
Coal tar	3,618	1,948,875	1,064,963
Belgium	2,447	1,298,412	621,880
Creosote oil	181,213	10,700,680	25,693,970
Germany	179,754	8,293,230	1,136,988
United Kingdom	.....	2,407,450	24,556,982
Dyes:			
Aniline and other	1,893,782	3,209,930	4,036,154
Germany	1,892,371	2,764,387	3,190,102
Switzerland	.....	144,917	240,250
United Kingdom	.....	28,239	361,735
United States		41,110	.....
Indigo, synthetic	74,913	693,567	1,207,590
Germany	74,913	692,773	1,137,867
Naphthalene	82,486	216,174	110,008
Phenol (carbolic acid)	...	247,740	137,158
United Kingdom	...	177,973	85,486
Saccharin	710	63,560	154,705
France	....	.....	53,707
Switzerland	90	.....	23,634
United Kingdom	.....	43,718	5,595
United States	....	15,415	58,510
Solvent naphtha	.....	85,978	42,240
United Kingdom	.....	85,978	42,240
Toluene and xylene	...	52,110	11,032
Other products	54,238	36,221,346	9,642,160
Germany	47,644	35,826,103	9,385,165
United Kingdom	.....	375,533	210,036
DYEING AND TANNING MATERIALS:			
Extracts used for dyeing:			
Extracts of dyewoods	950	942,904	216,350
France	.....	720,305	113,986
United Kingdom	...	151,497	.....
United States	816	37,210	.....
Indigo, natural	1,636	15,196	12,403
Madder and other natural dyes	65,418	235,654	209,534
Germany	65,418	136,560	136,967
United Kingdom	....	92,118	58,806
Synthetic dyes, n. e. s.	....	.....	16,914
Extracts used for tanning			
Liquid	278,812	5,787,035	4,405,968
Belgium	...	77,091	1,329,652
France	.....	2,510,818	1,223,515
Germany	278,812	262,176	589,090
United Kingdom	...	439,280	456,789
United States	.....	2,116,560	349,805
Solid:			
Gambier and cutch	.....	2,788,739	1,369,119
United Kingdom	.....	1,626,621	690,485
Dutch East Indies	.	937,317	673,854
Other	57,904	14,013,067	4,577,781
Belgium	....	1,369,273	767,125
United Kingdom	...	2,166,304	501,770
Argentina	57,369	5,656,084	1,394,525
Brazil	.....	870,522	223,044
United States	....	3,878,654	1,553,796
EXPLOSIVES:	Metric tons	Metric tons	Metric tons
Gunpowder	490,222	443,817	686,526
Germany	14,059	336,573	382,705
United Kingdom		104,334	217,142
Other (dynamite, etc.)	171,661	746,531	692,390
Germany	171,650	65,367	211,857
Norway	....	246,212	
United Kingdom	....	434,600	448,969
FERTILIZERS:			
Ammonium sulfate	39	1,378	10,131
Germany	39	1,337	9,495
Sweden	..		555
Bone ash and bone meal	2	5,052	1,374
Belgium	.	2,025	1,369
United Kingdom	.	2,763	..
Calcium:			
Cyanamide	17	120	178
Germany	17	120	166
Nitrate (Norway saltpeter)		4,126	45
Germany		35	25
Norway		4,016	.
Fertilizers, chemical, n. e. s.	10,604	4,370	7,021
Belgium	868	840	1,218
Germany	9,736	3,369	5,774
Guano, artificial	5	150	233
Nitrogenous fertilizers, organic	...	292	150
Phosphates, crude	40	29,184	114,876
Switzerland	...	3,451	
Algeria, Tunis	....	...	30,884
Chile	.		6,507
United States	.	25,327	77,379
Potash fertilizers:			
Kainite and carnallite	66,759	51,957	101,810
France		156	1,613
Germany	63,098	51,083	99,561
Manure salts	91,614	100,434	192,175
Germany	84,434	100,089	186,070
Muriate	53	3,011	2,785
Germany	21	3,011	2,753

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1918 Metric tons	1919 Metric tons	1920 Metric tons
FERTILIZERS (*Concluded*):			
Potash Fertilizers (*Concluded*):			
Sulfate	14,995	2,310	25,144
Germany	14,995	2,135	23,971
Slag, basic	2,338	90,752	160,167
Belgium	.....	55,978	123,532
France	.....	129	8,686
Germany	2,328	34,425	9,591
Luxemburg	.....	...	18,302
Sodium nitrate	1,128	151,301	155,273
Belgium	.....	1,139	11,804
Germany	.....	1	3,533
United Kingdom	.....	43,362	2,265
Chile	1,128	96,183	131,666
Peru	.....	...	5,950
United States	....	9,644	....
Superphosphate	50	2,891	30,170
Belgium	17	2,870	24,223
Tankage	1	535	379
Belgium	.....	525	379
OILS, VEGETABLE:	Pounds	Pounds	Pounds
Fixed:			
Castor	..	335,960	508,455
United Kingdom		235,723	140,262
Dutch East Indies	.	60,451	222,224
Colza (patent oil)		49,804	18,792
United Kingdom	.	27,758	18,336
Corn	..	.....	162,598
Cottonseed		43,778,610	19,514,490
Belgium	.	232,879	455,777
United Kingdom	..	12,250,306	7,690,538
United States		30,939,180	11,239,787
Coconut	3,012,885	139,317,195	114,171,145
Belgium	..	972,435	2,987,616
British India	..	3,063,000	374,094
Dutch East Indies	..	57,057,980	78,358,019
Japan and Korea	...	1,126,192	564,640
Philippines	..	55,829,112	24,639,113
United States		10,916,086	4,781,939
Linseed	33,336	2,632,017	2,137,342
Belgium	.....	735,521	681,195
United Kingdom	18,982	1,669,186	1,356,643
United States	8,525	186,665	14,972
Olive	.....	833,495	36,764
France	.....	55,367	20,468
Spain	...	709,796	8,400
Palm	1,443,192	9,177,283	15,732,150
Belgium	.....	149,233	2,595,416
United Kingdom	67,082	3,125,916	4,066,527
Belgian Congo	....	1,040,562	1,484,048
British West Africa	1,372,847	4,275,647	5,188,242
Palm-kernel	19,186,056	16,511,334	25,767,433
Belgium	.....	2,220,210	1,688,137
United Kingdom	19,186,056	14,054,615	22,281,425
Peanut	2,040,889	5,422,983	2,269,790
United Kingdom	2,039,527	282,483	370,600
Dutch East Indies	.....	5,055,292	1,236,690
Rapeseed	10,060,025	14,606,620	2,324,383
United Kingdom	10,047,346	14,034,688	1,642,675
United States	.....	488,807	455,497
Sesame	12,359,146	986,824	652,820
United Kingdom	12,359,146	986,824	221,723
United States	....	.....	208,504
Soy-bean	6,765,988	84,734,000	80,094,430
Belgium	.....	5,007,946	1,090,168
United Kingdom	6,765,988	17,788,944	3,498,519
China	....	10,036,803	14,605,808
Japan and Korea	.	34,562,912	55,097,295
United States	.	17,337,399	2,653,293
Volatile	...	828,488	486,035
France	.....	3,664	21,107
Germany	..	6,197	21,667
United Kingdom	....	444,769	177,053
Dutch East Indies	....	292,827	137,703
PAINTS, PIGMENTS, AND VARNISHES:			
Colors, prepared	307,161	1,668,967	2,444,695
Germany	281,987	559,017	779,848
United Kingdom	15,688	883,983	1,240,909
United States	.	169,780	197,966
Lakes	.	151,600	300,007
Germany	.	39,405	168,197
United Kingdom	..	71,558	79,620
United States		38,426	28,325
Lithopone	3,448,298	1,140,233	1,500,113
Germany	3,445,830	1,140,233	1,450,505
Paints and colors, n. e. s.	4,426,367	4,957,384	10,797,830
Belgium	16,045	94,200	590,052
Germany	4,279,308	3,399,093	6,952,878
United Kingdom	..	765,427	1,504,126
United States	17,968	105,230	326,756
Red lead (minium)	268,790	2,480,520	4,467,347
Belgium	.	10,368	628,247
Germany	261,263	1,541,064	2,721,498
United Kingdom	7,527	929,087	947,192
Varnishes and siccatives	10,088	513,964	721,359
Germany	3,230	27,869	83,372
United Kingdom	1,598	376,572	370,910
United States	.....	84,633	142,262
White lead	2,339	3,124,030	5,141,777
Belgium	....	444,012	889,554
Germany		2,041,132	2,594,852
United Kingdom	2,339	279,068	735,120
United States		399,663	899,213
Zinc white	158,345	17,867,460	21,852,157
Belgium	1,455	416,806	3,382,805
Germany	156,890	17,341,150	17,788,518
PERFUMERY AND COSMETICS:			
Perfumery, cosmetics, and toilet preparations	215,191	746,093	1,596,016
France	51,906	240,678	604,610

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS *(Continued)*

	1918 Pounds	1919 Pounds	1920 Pounds
PERFUMERY, ETC. *(Concluded)*			
Germany	83,057	209,648	597,730
United Kingdom	51,584	196,436	209,918
United States	3,311	68,416	106,862
Synthetic perfumes, solid or liquid	.....	62,739	127,619
France	.....	4,875	3,397
Germany	.....	22,137	92,155
United Kingdom	.....	28,958	16,001
United States	.....	5,913	2,992
OTHER PRODUCTS:			
Candles:			
Composition, spermaceti, and other sorts, n. e. s.	1,989	194,536	69,591
United Kingdom	.....	165,214	22,700
Stearin	68	75,991	102,045
United Kingdom	68	22,527	65,856
Wax	223	60,852	25,873
United Kingdom	.....	27,026	15,106
Gelatin and articles of gelatin	2,725	142,544	158,913
France	.....	3,732	26,409
Germany	1,825	104,210	52,075
United Kingdom	.....	18,100	24,363
United States	.....	11,277	23,905
Glucose:			
Liquid	.....	3,435,794	3,731,136
Belgium	.....	427,470	1,541,382
United States	.....	2,337,577	2,159,494
Solid	.....	24,577	99,208
Burnt (caramel)	.....	1,687	8,964
Glues:			
Bone, hide, and fish	10,068	533,605	640,620
Belgium	.....	137,083	178,180
France	.....	2,487	49,640
United Kingdom	.....	367,685	352,750
Other	.....	978,137	1,027,660
Belgium	.....	47,893	46,683
Germany	.....	476,833	605,770
United Kingdom	.....	314,015	335,413
Inks:			
Printing, dry or prepared	498,884	805,137	1,251,754
France	12,818	36,392	195,634
Germany	289,249	414,958	569,227
United Kingdom	196,817	252,645	312,265
United States	.....	98,822	141,036
Other	134,577	248,192	357,000
France	.....	7,026	68,835
Germany	131,133	196,864	210,410
United Kingdom	3,435	41,520	59,117
United States	.....	2,734	15,796
	Metric tons	Metric tons	Metric tons
Paper and pulp:			
Wood pulp:			
Chemical	30,530	17,936	38,197
Belgium	.....	11	1,964
Germany	2,351	252	4,369
Norway	4,212	3,356	4,981
Sweden	23,967	13,321	25,587
United States	.....	52	260
Mechanical	33,234	14,930	12,888
Finland	.....	.....	2,750
Norway	22,972	4,861	4,499
Sweden	9,768	6,379	4,973
	Pounds	Pounds	Pounds
Paper:			
Newsprint	4,203,618	8,739,310	16,370,154
Finland	.....	.....	5,830,093
Germany	1,099,769	4,101,268	9,851,767
Norway	2,943,233	2,552,175	600,169
Sweden	160,616	1,126,970	71,811
Printing and writing:			
Containing wood	8,593,184	8,820,969	27,905,120
Finland	.....	.....	3,065,470
Germany	604,075	4,649,183	22,054,810
Norway	7,436,054	2,111,036	1,172,438
Sweden	549,420	1,439,142	1,026,432
United Kingdom	.....	115,145	178,070
Not containing wood	2,584,276	4,446,278	28,590,197
Belgium	2,707	213,928	1,803,128
Finland	.....	.....	2,640,543
Germany	368,117	2,198,740	19,672,875
Norway	1,977,220	522,487	525,908
Sweden	4,969	242,350	829,793
United Kingdom	5,210	720,526	2,022,550
Wrapping, not printed	3,385,418	12,760,442	34,790,642
Belgium	88,095	108,423	430,065
Finland	.....	.....	991,048
Germany	314,789	9,604,437	32,433,277
Sweden	575,700	2,066,476	346,326
Norway	2,401,654	.....	.....
	Metric tons	Metric tons	Metric tons
Pitch	37,027	63,155	70,791
Belgium	2,046	19	1,959
Germany	885	15,995	10,764
United Kingdom	33,895	47,110	42,663
Canada	.....	.....	4,350
Mexico	.....	.....	10,492
	Pounds	Pounds	Pounds
Rosin	207,500	8,303,337	9,618,147
Belgium	.....	67,940	824,090
France	40,515	3,197,194	5,354,415
Spain	166,985	915,745	372,674
United States	.....	4,037,303	2,681,340
Soap:			
Perfumed, transparent, and liquid	5,256	1,463,726	1,368,718
Austria	.....	.....	123,869

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS *(Concluded)*

	1918 Pounds	1919 Pounds	1920 Pounds
OTHER PRODUCTS *(Concluded)*:			
Soap *(Concluded)*:			
Belgium	.....	29,593	151,618
France	518	20,278	166,634
Germany	.....	6,404	157,680
United Kingdom	.....	516,910	587,666
United States	.....	875,462	139,810
Hard, n. e. s., and non-perfumed soap powder	52,820	5,177,125	1,524,033
United Kingdom	4,158	4,811,015	784,927
United States	45,338	265,858	455,792
Soft, n. e. s.	1,616	67,788	153,790
Textile (hard and soft)	.....	25,838	12,630
	Metric tons	Metric tons	Metric tons
Sugar:			
Beet sugar, raw	.....	.....	888
Belgium	.....	.....	890
Cane sugar:			
Raw	3	47,584	40,408
Belgium	.....	.....	5,064
United Kingdom	.....	6,545	403
Dutch East Indies	3	15,383	383
Dutch Guiana	.....	151	2,677
Cuba	.....	20,630	22,961
Dominican Republic	.....	2,930	549
Peru	.....	1,852	796
British America	.....	37	6,165
United States	.....	.....	620
Refined	8	104	146
Dutch East Indies	.....	6	30
United States	7	96	106
Bastard sugar	.....	.....	662
United Kingdom	.....	.....	629
	Pounds	Pounds	Pounds
Tar, wood	836,780	5,345,900	3,838,770
Denmark	.....	1,790,374	266,693
Germany	784,755	1,257,827	122,092
Norway	.....	24,846	776,973
Russia, European	.....	777,085	.....
Sweden	51,753	1,314,560	2,189,030
Turpentine, and spirits of	154,341	6,989,900	6,821,024
Belgium	.....	1,312	465,768
France	.....	917,495	2,912,985
Spain	154,019	466,550	327,590
United Kingdom	.....	254,107	560,225
United States	.....	5,143,316	2,3268,90

THE EXPORT TRADE

In compiling the following table of exports it has been impossible to make a satisfactory comparison with the pre-war trade, for the reason already stated in connection with the table of imports. The export figures relate only to goods of domestic manufacture and to imported goods that have actually passed into Dutch hands before being reëxported. They do not include returns of goods passing directly through Dutch territory from one foreign country to another. The quantities represent gross weights.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1918 Pounds	1919 Pounds	1920 Pounds
CHEMICALS:			
Acetates:			
Calcium	.....	.....	265
Copper	.....	.....	187
Lead	.....	52,477	686,462
France	.....	46,791	323,403
Acetone	.....	703	4,482
Acids:			
Acetic	48,976	1,242,200	6,419,830
United Kingdom	.....	49,355	1,180,141
British India	.....	253,928	1,617,722
Dutch East Indies	46,700	657,511	2,120,714
Straits Settlements	.....	171,795	694,491
Hydrochloric	.....	108,328	310,250
Nitric	.....	33,094	96,505
Oleic, and other fatty acids	.....	14,955,732	48,916,370
Austria	.....	131,920	6,240,556
Belgium	.....	1,177,100	4,388,113
France	.....	.....	736,236
Germany	.....	4,828,980	27,003,320
United Kingdom	.....	8,218,820	8,161,490
Stearic and palmitic	.....	2,638,726	5,508,860
Belgium	.....	245,700	143,236
Denmark	.....	156,319	409,639
Finland	.....	.....	510,403
France	.....	623,120	123,069
Germany	.....	383,910	207,446
United Kingdom	.....	339,311	1,700,696
Sulfuric	.....	1,127,003	12,767,968
Rumania	.....	.....	1,388,449
Dutch East Indies	.....	48,303	2,722,682
Egypt	.....	952,979	4,308,789
Alum	26	9,751	130,460
Ammonia, liquid	.....	285,690	354,918
Ammonium chloride	.....	9,784	154,857
Calcium:			
Carbide	.....	22,635	455,894
Chloride	.....	1,385	34,840
Phosphate	55	1,979,707	1,509,545
Germany	55	1,979,019	594,983
United Kingdom	.....	.....	775,295
Chemicals, n. e. s.	2,157,236	10,737,746	15,283,908
Belgium	14,129	2,927,525	1,180,273
France	145,723	1,512,243	1,542,215
Germany	77,096	1,449,451	929,400
Spain	.....	222,314	1,407,208

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1918	1919	1920
CHEMICALS (*Concluded*):	Pounds	Pounds	Pounds
Chemicals, n. e. s. (*Concluded*):			
Switzerland	14,786	20,492	886,106
United Kingdom	1,013,613	1,790,914	5,733,883
Dutch East Indies	29,917	362,667	999,708
United States	298,543	1,493,107	1,653,665
Chloroform	.....	3,080	1,823
Cocaine	174	2,436	895
Copper sulfate	851	13,508	374,706
Ether, sulfuric	.....	29,174	26,553
Ethers, fruit	.....	395,514	473,440
Norway	.....	23,104	21,812
Sweden	.....	32,130	39,734
Dutch East Indies	.....	110,110	96,110
Japan and Korea	.....	12,114	29,123
Foods, chemical	2,749	66,392	35,968
Gases, compressed:			
Carbonic acid	1,113	182,979	1,231,890
Belgium	.....	48,363	545,966
Dutch East Indies	787	120,117	449,247
Other (oxygen, hydrogen, etc.)	3,086	181,588	260,930
Belgium	.....	121,995	41,877
United States	.....	.....	110,540
Glycerol:			
Crude	.....	142,965	1,621,015
United States	.....	133,536	1,302,996
Refined	1,971,325	1,464,557	3,286,895
Belgium	.....	253,386	471,249
Germany	.....	39,368	639,578
Sweden	.....	295,950	424,507
United Kingdom	1,743,843	43,190	285,556
United States	.....	.....	220,617
Iron sulfate	.....	9,976	30,686
Magnesia	79	1,822,770	9,949,928
France	.....	311,709	1,773,753
Germany	.....	27,183	606,388
United Kingdom	.....	829,050	3,533,375
United States	.....	.....	1,780,338
Medicines and drugs, n. e. s.	293,975	1,192,917	1,223,290
Belgium	1,000	298,014	404,300
France	.....	17,544	50,497
Dutch East Indies	161,129	533,757	418,929
United Kingdom	15,831	96,108	75,718
United States	53,255	90,063	66,920
Methanol	.....	1,184	225
Potassium:			
Hydroxide (caustic potash)	.....	26,213	245,628
Salts, n. e. s.	.....	348,657	1,263,654
Belgium	.....	300,109	951,433
Quinine and its salts	170,468	225,698	265,567
Germany	1,120	22	10,071
Greece	1,845	43,870	43,138
Italy	6,109	16,835	13,878
United Kingdom	125,412	20,298	17,123
China	.....	.....	38,768
United States	15,979	96,483	69,860
Sodium:			
Acetate	.....	48	163
Carbonate:			
Crystals	.....	49,403	47,421
Soda ash	3,389	50,480	253,474
Hydroxide (caustic soda)	485	66,952	1,215,556
Germany	.....	1,135	1,060,904
Nitrate, refined	6,146	320,470	1,214,270
France	.....	.....	402,683
Spain	.....	56,967	247,930
United Kingdom	.....	.....	369,171
Sulfate (Glauber salt)	.....	4,337,290	2,906,144
Belgium	.....	2,264,588	2,777,824
Tetraborate (borax)	791	6,226	372,400
Germany	.....	1,193	290,050
COAL-TAR PRODUCTS:			
Asphalt	.....	535,439	620,484
Benzene	.....	8,148	291,760
Germany	.....	5,803	287,511
Carbolineum	13,316	261,523	240,981
Dutch East Indies	12,787	193,504	132,339
Coal tar	12,809,120	226,018	2,154,960
Dutch East Indies	.....	114,110	1,180,685
Belgium	12,687,602	.....	.....
Dyes:			
Aniline and other	3,212	725,446	351,252
France	.....	8,062	40,179
Germany	3,146	.....	24,220
United Kingdom	.....	21,226	108,483
Dutch East Indies	.....	668,580	53,731
United States	.....	20,876	21,923
Indigo, synthetic	.....	7,414	35,556
Naphthalene	6,790	98,551	382,423
United States	.....	.....	285,578
Phenol (carbolic acid)	168	89,990	102,300
Saccharin	4,777	7,886	153,680
Austria	.....	.....	15,620
Czechoslovakia	.....	.....	15,975
Hungary	.....	.....	19,112
Sweden	2,780	1,691	16,865
Switzerland	.....	324	40,047
Solvent naphtha	.....	.....	20,565
Toluene and xylene	.....	710	16,345
Other products	445	18,280,126	315,228
Germany	.....	1,091	77,162
Dutch East Indies	.....	137,877	165,823
United States	.....	18,054,840	.....
DYEING AND TANNING MATERIALS:			
Extracts used for dyeing:			
Extracts of dyewoods	.....	51,066	26,431
Indigo, natural	.....	342	1,660
Madder, and other	.....	96,047	39,685
United Kingdom	.....	16,407	38,590
Synthetic dyes, n. e. s.	.....	.....	24,290

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1918	1919	1920
DYEING AND TANNING MATERIALS (*Concluded*):	Pounds	Pounds	Pounds
Extracts used for tanning:			
Liquid	.....	72,567	617,169
Belgium	.....	26,081	344,190
Germany	.....	39,904	258,047
Solid:			
Gambier and cutch	.....	28,027	87,614
Other	.....	1,292,848	1,424,362
Germany	.....	1,267,182	1,218,780
EXPLOSIVES:			
Gunpowder	175,117	247,160	321,500
Dutch East Indies	175,117	246,631	320,775
Other (dynamite, etc.)	70	31,844	8,353
Dutch East Indies	.....	14,065	8,153
	Metric tons	Metric tons	Metric tons
FERTILIZERS:			
Ammonium sulfate	.....	840	10,892
Belgium	.....	.....	1,398
France	.....	400	.....
Spain	.....	.....	6,117
Dutch East Indies	.....	440	1,993
French America	.....	.....	703
Bone ash and bone meal	76	4	2,900
Finland	.....	.....	900
United Kingdom	76	.....	703
Calcium nitrate (Norway saltpeter)	.....	.....	2,982
Belgium	.....	.....	2,753
Fertilizers, chemical, n. e. s.	595	646	8,040
France	.....	25	1,505
Dutch East Indies	.....	320	1,447
United States	.....	.....	2,546
Guano, artificial	.....	586	161
United States	.....	.....	161
Nitrogenous fertilizers, organic	.....	460	1,092
United States	.....	251	475
Phosphates, crude	.....	.....	20
Potash fertilizers:			
Kainite and carnallite	.....	.....	1,636
United States	.....	.....	1,610
Manure salts	.....	.....	1,682
United States	.....	.....	1,600
Muriate	.....	1,635	1,684
United States	.....	1,189	818
Sulfate	.....	1,311	1,161
Spain	.....	186	246
French America	.....	.....	450
United States	.....	1,100	314
Slag, basic	.....	63	181
Sodium nitrate	.....	7	560
Superphosphate	.....	400	63,350
Belgium	.....	.....	2,500
Denmark	.....	.....	5,000
Germany	.....	.....	15,543
Spain	.....	.....	21,019
Dutch East Indies	.....	400	2,037
Egypt	.....	.....	5,884
Union of So Africa	.....	.....	6,883
Tankage	.....	.....	1,109
Belgium	.....	.....	1,109
OILS, VEGETABLE:	Pounds	Pounds	Pounds
Fixed:			
Castor	48,597	18,748	236,695
Germany	.....	1,812	155,200
Coconut	.....	59,525,347	128,557,212
Austria	.....	.....	11,625,933
Belgium	.....	19,499,381	26,790,226
Czechoslovakia	.....	.....	3,020,178
Denmark	.....	417,368	2,994,225
Germany	.....	11,724,733	75,507,185
Switzerland	.....	1,342,443	1,334,030
United Kingdom	.....	26,499,928	4,910,146
Colza (patent oil)	201	76,630	42,097
Corn	.....	1,477	516,260
Belgium	.....	926	420,490
Cottonseed	.....	12,816,111	5,482,950
Belgium	.....	1,024,113	673,840
Germany	.....	1,576,069	3,922,270
United Kingdom	.....	10,206,782	223,108
Linseed	157,930	38,170,606	59,239,275
Austria	.....	1,168,326	2,049,157
Belgium	.....	2,995,041	4,133,925
Czechoslovakia	.....	.....	2,149,976
Germany	.....	22,118,242	30,848,480
Sweden	.....	829,250	364,589
Switzerland	.....	1,380,753	2,759,590
Dutch East Indies	155,926	2,246,156	8,673,952
United States	.....	2,769,861	3,893,962
Olive	46	396,407	36,162
United Kingdom	.....	320,780	21,056
Palm	.....	235,143	168,184
Palm-kernel	.....	10,872,428	8,893,340
Belgium	.....	1,833,578	1,924,953
Germany	.....	271,243	6,489,732
United Kingdom	.....	5,754,803	121,505
Peanut	48,396	5,641,787	8,702,770
Belgium	.....	1,670,436	987,759
Denmark	.....	291,292	1,046,730
France	.....	160,640	819,604
Germany	.....	905,055	961,057
Norway	.....	379,449	2,611,470
Sweden	.....	570,212	637,698
Switzerland	.....	874,014	764,298
United Kingdom	.....	548,590	282,652
Dutch East Indies	48,396	197,168	248,410
Rapeseed	434	9,599,890	7,821,248
Belgium	.....	2,956,482	3,004,527
Germany	434	1,253,195	4,298,310
United Kingdom	...	5,298,517	107,378

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1918 Pounds	1919 Pounds	1920 Pounds
OILS, VEGETABLE (*Concluded*):			
Fixed (*Concluded*):			
Sesame	22	6,019,757	5,622,825
Belgium	.....	538,644	1,877,580
Denmark	.....	132,290	479,567
Germany	.....	4,706,865	2,298,074
Sweden	.....	490,427	565,353
Soy-bean	.....	14,813,565	26,766,456
Austria	.....		2,829,420
Belgium	.....	7,252,120	10,476,215
Germany	.....	3,418,353	8,811,310
United Kingdom	.....	3,627,800	3,384,042
Volatile	.....	392,864	354,464
France	.....	35,744	13,032
Germany	.....	122,584	50,860
Sweden	.....	34,194	19,491
United Kingdom	.....	61,100	64,300
United States	.....	42,126	17,857
PAINTS, PIGMENTS, AND VARNISHES:			
Colors, prepared	395,290	4,341,572	6,681,080
Belgium	.....	211,642	384,574
Denmark	39,320	184,902	107,215
Germany	.....	195,625	310,843
Norway	22,979	195,572	99,558
Spain	.....	138,607	134,312
United Kingdom	83,105	285,739	427,770
Dutch East Indies	217,268	2,316,771	4,156,917
Argentina	12,412	198,958	130,123
United States	12,740	141,398	81,355
Sweden	.....	88,328	134,411
Lakes	.....	2,640,415	4,617,075
Belgium	.....	287,174	413,673
Sweden	.....	146,217	190,634
United Kingdom	.....	616,472	1,208,378
Dutch East Indies	.....	83,050	634,704
Argentina	.....	116,175	602,554
United States	.....	240,220	635,580
Lithopone	2,920,046	12,493,806	27,157,673
Belgium	.....	839,630	19,187,260
France	.....	2,879,810	3,897,496
United Kingdom	2,802,210	7,666,072	3,859,888
United States	.....	951,526	.....
Paints and colors, n. e. s.	915,518	5,924,883	9,273,830
Belgium	.....	859,809	2,187,303
Greece	.....	225,282	404,323
United Kingdom	191,240	336,850	763,320
Dutch East Indies	162,020	3,146,358	3,793,603
United States	.....	172,230	160,124
British America	261,413	77,898	.....
Red lead	36,705	850,620	1,627,964
France	.....	882	426,830
Dutch East Indies	32,148	552,412	713,652
Varnishes and siccatives	33,182	791,003	883,163
Denmark	16,376	108,893	78,454
Germany	.....	200,623	56,840
Sweden	.....	74,518	107,500
Dutch East Indies	.....	154,680	218,158
White lead	4,226	174,734	538,547
Dutch East Indies	.....	37,679	307,124
Zinc white	158,990	8,238,726	8,876,954
Belgium	.....	899,300	4,271,945
France	.....	3,201,112	2,747,775
United Kingdom	72,752	3,341,156	100,707
Dutch East Indies	79,432	618,344	1,443,050
PERFUMERY AND COSMETICS:			
Perfumery, cosmetics, and toilet preparations	192,113	1,008,729	804,694
Dutch East Indies	20,549	895,809	588,215
Synthetic perfumes, solid or liquid	.....	107,427	369,561
Germany	.....	6,951	10,908
United Kingdom	.....	9,857	70,687
China	.....	8,697	32,024
Japan and Korea	.....	4,925	30,005
Dutch East Indies	.....	4,561	16,350
United States	.....	20,909	51,952
OTHER PRODUCTS:			
Candles:			
Composition, spermaceti, and other sorts, n. e. s.	.....	1,403,912	2,455,850
Greece	.....	419,273	413,380
Spain	.....	.....	260,862
Turkey, European	.....	126,484	267,582
Egypt	.....	125,483	317,395
Morocco	.....	29,207	453,094
Stearin	2,434	1,374,190	1,457,937
Germany	.....	672,864	31,032
Greece	.....	35,505	87,098
Norway	.....	210,910	252,264
Sweden	.....	121,380	325,808
Egypt	.....	44,159	134,769
Wax	132	1,270	2,467
Gelatin and articles of gelatin	176,387	1,025,637	1,565,615
Belgium	.....	29,315	54,254
United Kingdom	1,146	195,930	57,093
United States	160,320	585,153	1,368,030
Glucose:			
Liquid	150	63,996	1,992,743
Italy	.....	.....	1,614,445
Norway	.....	44,136	6,956
United Kingdom	.....	.....	220,927
Solid	.....	26,632	440,225
Germany	.....	22,223	4,616
Italy	.....	.....	378,739
Burnt (caramel)	.....	60,160	101,889
Glues:			
Bone, hide, and fish	783,843	2,622,580	2,765,463
Belgium	.....	282,483	655,400
Germany	.....	1,358,043	394,120
United Kingdom	6,724	151,347	528,942

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

	1918 Pounds	1919 Pounds	1920 Pounds
OTHER PRODUCTS (*Concluded*):			
Glues (*Concluded*):			
China	.....	11,000	227,749
Japan and Korea	.....	229,390	493,660
Dutch East Indies	7,458	220,970	207,098
Norway	733,255	137,635	66,326
Other	.....	197,878	472,717
Belgium	.....	36,614	60,667
Germany	.....	63,270	121,387
Dutch East Indies	.....	38,105	75,985
Inks:			
Printing, dry or prepared	26,266	173,746	333,008
United Kingdom	.....	45,772	112,822
United States	.....	64,068	.....
Dutch East Indies	.....	12,901	55,676
Germany	.....	3,563	85,321
Other	52,684	590,215	1,082,930
Dutch East Indies	10,468	386,574	827,767
Argentina	2,205	45,851	60,521
	Metric tons	Metric tons	Metric tons
Paper and pulp:			
Wood pulp:			
Chemical	.....	81	86
United States	.....	50	.....
Mechanical	20	.....	211
United States	.....	.....	200
	Pounds	Pounds	Pounds
Paper:			
Newsprint	557,765	18,859,689	22,044,680
Belgium	557,765	14,590,486	7,480,092
France	.....	14,275	2,376,675
Greece	.....	79,472	543,631
United Kingdom	.....	3,235,398	4,705,623
Dutch East Indies	.....	344,353	513,170
Union of So. Africa	.....	.....	705,005
Australia	.....	.....	3,679,967
Chile	.....	.....	728,537
Printing and writing:			
Containing wood	115,912	4,645,247	6,825,764
Belgium	12,075	2,191,575	1,158,697
United Kingdom	17,835	1,301,779	1,545,048
Dutch East Indies	81,443	602,850	2,547,653
Not containing wood	900,284	9,572,382	14,230,425
Belgium	.....	1,765,832	469,282
France	82,087	315,543	243,168
Greece	.....	476,756	872,204
Portugal	.....	107,034	266,003
Spain	.....	147,626	459,390
Sweden	2,425	86,243	317,666
United Kingdom	68,330	428,665	1,800,000
British India	.....	19,861	323,603
Dutch East Indies	392,407	5,074,037	6,872,470
Argentina	.....	256,748	332,120
Brazil	28,477	453,495	802,791
Wrapping, not printed	5,773,487	11,026,430	22,934,355
Belgium	.....	1,891,925	1,468,051
Greece	.....	813,726	1,763,976
Turkey, European	274,394	993,303	1,678,220
United Kingdom	581,584	2,339,854	7,683,078
British India	.....	.....	.....
Dutch East Indies	245,723	1,059,230	1,615,120
Egypt	1,984,440	782,875	1,292,409
British America	955,402	1,373,094	1,911,807
	Metric tons	Metric tons	Metric tons
Pitch	.....	74	618
	Pounds	Pounds	Pounds
Rosin	22	259,303	63,594
Soap:			
Perfumed, transparent, and liquid	16,984	477,130	951,843
Belgium	.....	37,278	109,360
Germany	.....	322,117	74,518
Dutch East Indies	16,510	88,008	569,100
Hard, n. e. s., and non-perfumed soap powder	696,877	5,566,166	7,762,672
Belgium	.....	368,734	174,714
Czechoslovakia	.....	.....	589,457
Denmark	.....	60	428,766
Germany	694,170	4,982,532	2,238,460
Norway	.....	64	1,111,659
Poland	.....	.....	1,533,956
Sweden	.....	.....	480,978
Dutch East Indies	.....	106,217	554,015
Soft, n. e. s.	41,237	287,520	505,462
Dutch East Indies	36,800	239,526	422,849
Textile (hard and soft)	.....	.....	.....
	Metric tons	Metric tons	Metric tons
Sugar:			
Beet sugar, raw	13,018	4,615	16,665
Belgium	.....	1,941	.....
France	.....	202	.
Germany	2,024	2,250	9,400
Spain	.....	.....	1,323
Switzerland	.....	202	3,954
United States	.....	.....	1,977
United Kingdom	10,995	.....	.....
Cane sugar:			
Raw	1	2,865	51
Belgium	.....	958	.....
France	.....	1,136	.....
Germany	.....	768	51
Refined	10,127	31,638	59,372
Belgium	72	351	4,241
Germany	19	5,673	17,394
Spain	.....	.	2,758
Switzerland	2,575	1,725	21,616
United Kingdom	6,070	18,095	1,063
Turkey, European	.....	.....	3,676
British West Africa	.....	.....	1,170
United States	.....	609	2,554
Bastard sugar	.....	.....	39
	Pounds	Pounds	Pounds
Tar, wood	320	156,753	133,680
Turpentine, and spirits of	194	357,334	89,929

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

Vacuum Drying[1]

By Charles O. Lavett and D. J. VanMarle

BUFFALO FOUNDRY AND MACHINE COMPANY, BUFFALO, N. Y.

The manifest advantages of removing moisture from materials in a vacuum, long established as a successful laboratory practice, became applicable to commercial drying when it was found possible to design and construct apparatus of suitable size and strength to meet the peculiar and special problems which the creation and maintenance of a vacuum on a large scale entail.

Vacuum rotary and vacuum shelf dryers were the first to be successfully employed for commercial purposes, and it is proposed to discuss in this article the features of each of these types, as well as of the vacuum drum type. However, before entering upon this analysis it is desirable to point out those general characteristics which apply equally to all vacuum dryers, and which tend to differentiate them from other types.

THE FIELD OF VACUUM DRYERS

It is frequently assumed by those not familiar with drying under reduced pressure that vacuum dryers may be successfully applied to all materials. The fact is that vacuum drying, while its utility comprehends an extensive field, is by no means of universal application. Other dryers, such as the direct heat rotary, tunnel, spray, compartment, and atmospheric drum types, have their own, and oftentimes exclusive, fields. However, in many instances the fields overlap, and in still others the vacuum process enjoys a special preëminence. In any event, every drying problem merits study and investigation before a particular process is adopted in order to determine two vital considerations, namely, the quality of the dried product and the cost of its production. All too frequently these considerations are ignored, and a purchaser to his sorrow has been governed by an attractive low initial cost for which he has obtained in the long run a costly process.

Generally speaking, the principal advantages of vacuum dryers are:

Low cost of operation, including power and fuel consumption.
Drying at extremely low temperatures.
No overheating of sensitive materials.
Absolute temperature control.
A clean, sanitary medium free from obnoxious odors.
Uniformity of product at any preferred degree of dryness.
Absolute dryness when desired.
Economy of floor space.
Independence of climatic conditions.
Solvent recovery when desired.
Elimination of fire risk.

These points often go to the heart of a drying problem and govern its ultimate destiny. With such a problem the vacuum process is primarily concerned, and it is therefore with these considerations in mind that we must proceed to our examination of vacuum processes.

LIMITATIONS OF THE VACUUM DRYER

Vacuum drying systems comprehend, generally speaking, a suitable shell or casing with a condenser for the condensation of water vapors, and a vacuum pump for the removal of noncondensable gases. The shell or casing must be airtight, and its outer walls of sufficient strength to resist external atmospheric pressure. In fact, strength and workmanship in a degree often unnecessary and useless in other systems are imperative to vacuum processes and determine that their initial cost shall be considerably greater than that of the corresponding types of atmospheric dryers. Also the airtight casing requires that a vacuum drying system shall be operated on the batch principle, and, generally speaking, makes *continuous operation* impossible, except in case of the vacuum drum dryer. The same fact limits to a certain extent the size of the equipment and makes it less suited for the drying of materials in large bulk, such as fruits and vegetables, or of products of little value which are not injured by high temperatures, and where the requirements of quality or of uniform and low moisture content are not imperative. In fact, where vacuum processes are found to be disadvantageous it is usually due to the mechanical limitations of size inherent in the design of the apparatus, and it is very interesting, in this regard, to consider the advances which have been made in overcoming these limitations. At the present time, vacuum dryers are especially suitable for the drying of organic substances and other materials requiring rapid evaporation at low temperatures.

PRINCIPLE OF VACUUM DRYERS

The governing principles of the system are the reduction of the boiling point of a liquid under diminished pressure and the accelerated rate of evaporation at the boiling point. Reduction in pressure not only causes drying to occur at or above the boiling point of water, but increases the temperature difference between the heating medium and the material, thereby providing a better heat transmission. So successfully have difficulties of mechanical construction been met, that in a commercial system of large dimensions a vacuum of 28 to 29 in. is now attained, with a corresponding boiling point of water of 100° to 75° F. Accordingly, comparatively little heat is required to raise a material from which moisture is to be removed to a temperature most favorable for drying. At this temperature, assuming that the moisture to be removed is on the surface of the material and that it is in sufficient quantities, the rate of evaporation of the water is governed by the rate at which heat is transmitted to the material, as well as by the rate at which the vapors are removed.

---

[1] Presented at the Drying Symposium before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

Naturally, surface action and the absorption of moisture by the material exercise their usual restraining influence, and evaporation is not so great as would prevail if pure water were boiled under the same conditions.

Coincident with this accelerated evaporation is the problem of an accelerated removal of vapors from the vacuum chamber. The rate of this removal is of vital importance, for it is to be recalled that, whereas 1 lb. of water at 212° F. forms 26.8 cu. ft. of steam under atmospheric conditions, the same amount of water at 28 in. of vacuum forms 350.75 cu. ft., and under 29 in., 709.3 cu. ft. of steam. A difference of 1 in. of vacuum as expressed in the mercury column at 28 and 29 in., respectively, practically doubles the bulk of the vapor. The vacuum pump alone cannot cope with this large volume of vapor, and at the same time maintain a high vacuum, and it is therefore necessary to place between the dryer chamber and the pump a suitable condenser, whose performance, being substantially the reverse of that of the dryer, condenses the water vapors as rapidly as they are formed, and permits a high vacuum to be created. The vacuum then depends upon the vapor pressure of the condensate and the pressure exerted by the noncondensable gases which are in the materials, and in the cooling water in case a barometric condenser is used. The proper construction of a condenser to cope with these large volumes of vapors under low pressures with a comparatively low temperature difference between the vapor and the cooling water, is a problem in itself. And as a matter of fact, under practical commercial conditions, in the case of materials of high moisture content where the rate of evaporation is correspondingly high, a vacuum of 28 to 29 in. is usually not maintained, but is lowered slightly at the very beginning of the operation by reason of the large amount of noncondensable gases liberated at this stage, which amount varies with the material and with the temperature difference between material and heating medium. The presence of these gases naturally reduces the condensing capacity of the condenser. On the other hand, as soon as the moisture content in the material is lessened, the rate of evaporation is decreased on account of the influence of the surface action of the material, which gradually increases until it finally becomes the governing factor. This surface action soon establishes the vacuum at its maximum degree, while concurrently heat transmission operates disproportionately to the rate of evaporation, and thereby automatically raises the temperature of the material. Therefore, this harmful tendency is checked and partly neutralized by the higher vacuum and temperature. These aforementioned principles clearly define how the application of a vacuum greatly increases the rapidity of drying, and to a degree that often warrants the comparatively high initial expense of the equipment.

In the case of materials where moisture is partly confined in the interior of the material, changes in the surface are entirely prevented by virtue of the low temperature maintained in conjunction with the absence of air, whereby surface oxidation is practically eliminated. Rubber has been dried successfully by the vacuum process for years, and meat is still another instance of the utility of the vacuum system in overcoming difficulties of this nature. Other materials, such as gunstocks, electrical heaters with cemented joints, etc., are subject to warping or cracking due to too rapid removal of the moisture from the surface layer, which causes an unequal expansion between the center and the exterior. This problem has been solved by heating in a vacuum chamber under atmospheric pressure, thereby obtaining a uniform temperature throughout the objects to be dried, and applying vacuum for a very short time at intervals for the removal of vapor liberated during the heating and evacuating period.

Finally, the removal of water of crystallization, owing to the low vapor pressure of the crystals, is a slow process. Wherever possible the temperature should be raised to the point at which the water is liberated, but unfortunately this often results in fusion of the crystals.

Application of Heat

As no direct contact between a heating medium and a material is possible, vacuum dryers employ indirect heating. Heat is transmitted through a metal partition, on one side of which the heating medium is confined. This medium is usually saturated steam, which is very effective, in that its latent heat of evaporation can be advantageously obtained. In fact, from the laws of heat transmission it is evident that the rate at which heat is transmitted from saturated steam to the metal is more than ample for the requirements of the drying process. For low temperatures hot water, and for high temperatures circulating oil may be substituted as a heating medium for steam. In these instances, evaporation is considerably reduced, because a comparatively large amount of fluid is required to provide the latent heat necessary to evaporate the moisture. Furthermore, heat transmission by a fluid is influenced by the velocity of the liquid over the heating surface, and this velocity is limited by the construction of the dryer.

Whatever the heating medium, temperature control is readily obtained by simple and automatic methods. In fact, this is a very important adjunct to the vacuum system.

While the usual laws of heat transmission apply to the side of the heating surface contingent to the heating medium, these laws do not apply to the side adjacent to the material, because there is only imperfect contact between the material and the metal, a circumstance which greatly reduces the active heating surface. Of course, the extent of this surface varies with different products, and will in a great measure depend upon the coarseness and form of the materials under consideration. It should be noted in passing that, given the same area of active heating surface, transmission is, on some products, as much as four times greater in the rotary than in the shelf type of vacuum dryer, for in the former agitation continuously brings fresh material into contact with the heating surface.

HEAT LOSSES—The manner in which heat is applied in a vacuum dryer makes clear that, save where lost by radiation, all heat is utilized for heating the material and removing the moisture. Where hot water or circulating oil is utilized as a heating medium, heat units contained therein are conserved as the water or oil is returned to the heating system; where steam is employed heat losses are eliminated by returning the condensate to the boiler. In any event, losses due to radiation can be greatly reduced by insulating the dryers.

However, these heat losses are not very great, on account of the comparatively low temperatures at which vacuum dryers are operated. Generally speaking, the heating surface is in the interior of the dryer, and radiation is limited to heat transmission of the water vapor to the walls of the machine and at the few points of actual contact between the heating surface and the wall.

Heat conservation and economy as outlined above considerably reduce operating expense and offset, to some extent, the necessary expense of cooling water and power for the vacuum pump. Steam consumption of the vacuum dryer itself amounts to approximately 1.25 lbs. for each pound of water evaporated.

Absence of contact between the heating medium and the material gives rise to a further important consideration in vacuum drying, namely, the removal of any danger of injury or contamination from this source. Operation at low temperatures and accurate control of these temperatures make possible the protection of materials from injuries due to excessive or prolonged heat, and this is accomplished without sacrificing heat economy although, of course, at very low temperatures the capacity of the dryers is reduced through decreased heat transmission.

This is an opportune time to refer to the striking and peculiar advantage of the vacuum system in its entire independence of climatic conditions. To produce a very dry product of uniform moisture content without regard to seasonal or climatic conditions is at times a consideration of prime importance.

TEMPERATURE EMPLOYED—In order to reduce the drying period as much as possible, and by reason of the fact that heat transmission increases with the difference in temperature which prevails between the heating medium and the material, the highest possible temperature that the material will stand without injury is employed. In the beginning the temperature of the material will be low as a result of the high rate of evaporation, but as soon as the rate of evaporation drops the temperature of the material will rise. This begins as soon as the moisture content of the material falls below 15 to 20 per cent. Some materials, like pepsin, are more sensitive to heat the higher the moisture content and permit an increase of the temperature as drying proceeds.

For materials that produce a quantity of dust, a dust collector is placed between the dryer and the condenser. This class of materials is usually handled in the rotary type of dryer, and the dust-collecting device not only prevents the loss of material, but protects the condenser and the valves of the pump.

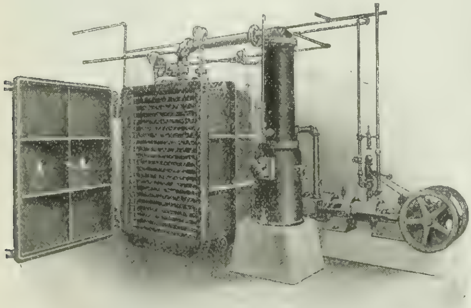


Fig. 1

Condensers

Condensers are either of the barometric type in which vapors are condensed by the injection of cold water, or of the surface type wherein the cooling water and vapor are separated by a metal wall. On account of the great volume of vapors to be handled, and their high velocity, the surface condensers have a very large cooling surface. The barometric condenser is usually installed with the rotary dryer; the surface condensers with shelf dryers, from which a smaller amount of vapor per unit of time is developed. The surface condenser also finds application in case solvents other than water are contained in the material. The condenser is usually placed on the top of a small receiver which can be closed off and discharged without interrupting the operation of the dryer. Where solvent recovery is desired, such solvents have a higher vapor pressure than water, and losses therefore would be excessive, for which reason the exhaust of the pump is discharged into an expansion tank connected to a small atmospheric surface condenser in which the remainder of the solvent is condensed, allowing a recovery of 95 per cent or more of the solvent contained in the material.

Vacuum Shelf Dryer

The dryer proper consists of a chamber of varying dimensions provided with a door at one end, or in the larger sizes, at both ends. The doors are usually hinged and include one or more observation glasses. Of special moment is the inclusion of heavy, molded rubber gaskets, whereby the door is made to fit tightly against the chamber. The dryer casings are of two types and consist of either a cylindrical chamber of welded or riveted steel boiler plate, with cast-iron heads and doors, or a rectangular chamber of cast iron. While the latter construction is the more expensive, by reason of its absence of riveted seams, it is the more reliable and less liable to leak.

SHELVES—Hollow steel heating shelves through which steam, hot water, or oil may be circulated, are spaced equidistantly in the interior of the casing. The material to be dried is placed in flat shallow pans or trays which rest on the heating shelves. In this connection, the varying width of the several heating shelves in the cylindrical type, in contrast with the rectangular type, makes it impossible to utilize the heating surface to the same extent, and unless special sizes of pans are employed, there will be, in the case of at least part of the shelves, a wasted surface where a pan or tray cannot be fitted in. In any event, in the vacuum shelf dryer the material is not, except in special cases, in direct contact with the heating surface. Heat is transmitted through the wall of the steel shelf to the contact surface of the tray resting on the shelf and thence to the material in the pan or trays. Heat transmission is uniform over the entire surface, provided the shelves are perfectly flat and level and without any rivets protruding above the surface. If the shelves which are connected to manifolds for equal distribution of the heating medium are not accurately flat and level, not only will there result a very vital interference with heat transmission, but where steam is employed as a heating medium, the shelves will not properly drain. Proper construction of the shelves is therefore indispensable, for shelves with these irregularities so reduce the contact surface between the pans and the shelf that uneven heating and drying results, a disability which may also be caused by warped pans. This situation is aggravated by the fact that, since a vacuum greatly retards heat transmission, overheating of the material results at points of actual contact, and where no contact is had, there is practically no transmission of heat whatever. The results are self-evident, in that the drying period is prolonged and a material of uneven moisture content is produced. Whatever conditions prevail, however, it is essential to the maintenance of an even and uniform supply of heat that the oil or hot water circulating system or steam traps, as the case may be, should be kept at all times in good working condition.

APPLICATIONS AND DISADVANTAGES—The shelf dryer has a wide range of adaptability, as, for example, its utilization for extracts, pastes, chemicals, and similar products of solid or semisolid consistency; or for materials that cannot be agitated, as, for example, gunstocks and pastes; or for products that can be successfully handled only at low temperatures, as for example, pepsin, glands, effervescent salts, etc.; or again, for those substances whose surfaces are liable to changes when drying, such as meat and rubber. Of its general disadvantages the most important are that its operation is not continuous, and that considerable labor is necessary to the loading and unloading of the pans and trays; and that considerable time is required for charging and discharging the dryer, though this last objection may, in given cases, be partly remedied by introducing the

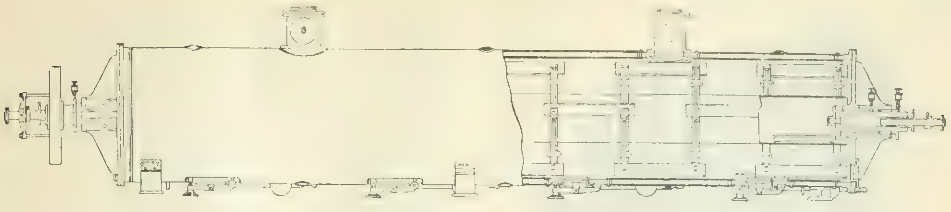


Fig. 2

pans into the dryer on trucks which have racks on a level with the dryer shelves. It may be stated as a rule that, for materials containing a moderate amount of moisture, heat losses are high in proportion to the small amount of water evaporated, and it is therefore imperative if heat losses are to be reduced to a minimum that the casing of the dryer always be properly insulated. Finally, liquids such as logwood extract are successfully handled in the shelf dryer, though there is a tendency in some cases for a small amount of the material to splash out of the shallow pans or trays. While a product of superior value can be produced at less cost on the vacuum drum dryer, the shelf dryer is generally used because the trade demands a finished product in the form of crystals.

Except for materials that are likely to foam, the vacuum shelf dryer requires but little supervision. In many instances the vacuum maintained on equipment in the field after operating a few months is reduced as a result of neglect of stuffing boxes, leaky valves, gaskets, etc. The following data illustrate the running expense of drying rubber.[1] It must be noted that this dryer had been in operation for years before the test was made and that the test run is representative of the daily performance of the apparatus:

Floor space of equipment, including working space	304 sq. ft.
Duration of test	3 hrs.
Steam pressure	3 lbs.
Vacuum	27.1 in
Temperature of rubber at start	118° F
Temperature of rubber at finish	180° F
Percentage of moisture evaporated	17.7
Weight of dry rubber	740 lbs.
Steam consumption per lb. of water evaporated	1.2 lbs.
Weight of dry rubber per sq. ft. pan surface	1.3 lbs.
Steam consumption per lb. of dry rubber	0.259 lb
H. p. of vacuum pump	9.25
Cost	
192 lbs. of steam at 40 cts. per 1000 lbs.	$0.0768
20.712 k.w. hrs. at 1.5 cts. per k.w. hr.	0.3107
690 gal. of water at 6 cts. per 1000 gal.	0.0414
	0.4289
Labor	
Filling pans	0.7600
Loading dryer	0.1748
Unloading dryer	0.1122
Emptying pans	0.6068
Total cost of labor	1.6538
Total	2.0827
Cost per lb. of dry rubber	0.002814
Cost per ton of dry rubber	5.628

Vacuum Rotary Dryer

The vacuum rotary dryer is utilized for such solids and semisolids as require or permit agitation, as, for example, starch, reclaimed rubber, compounding ingredients, tobacco, resinates, sulfur black, and other dyes. The dryer consists of a cylindrically jacketed casing with a centrally located heating tube extending throughout the entire length of the dryer, on which the agitator is mounted, permitting the mixing and better distribution of the material, which in this type of dryer comes into direct contact with the heating surface. Better heat transmission is therefore attained than in the shelf dryer. However, many products do not permit agitation, others form into large lumps which retain their moisture tenaciously, and still others tend to coat the heating surface of the dryer. The field of the rotary type is therefore somewhat more limited than is generally supposed. However, this dryer is especially applicable to products subject to oxidation during the drying process, or to autoxidation after discharge from the dryer, inasmuch as the charge can be cooled in the dryer before it is permitted to come in contact with the air.

The heating medium circulates not only through the center tube but also through a jacket, which latter may in some cases be omitted and the dryer heated by passing flue gases around it. Labor charges are lower than for the shelf type, as the dryer can be readily charged by means of a mechanical conveyor, or by a gravity flow from a hopper or bin placed above the dryer. The dryer requires little supervision, and one man can readily supervise the operation of six of the largest sized dryers.

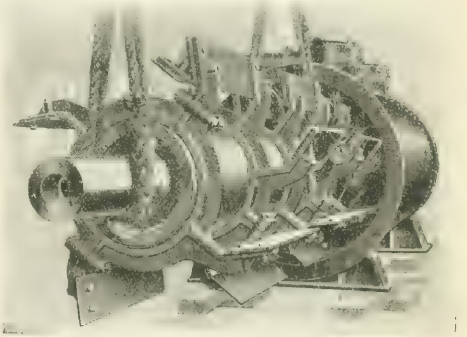


Fig. 3

The following data cover a test made with reclaimed rubber after the dryer had been in operation for about three years. This equipment, like the shelf dryer, was not gone over previous to making the test, the object being to determine running expense under prevailing plant conditions.

Duration of test	4.87 hrs.
Steam pressure	18.15 lbs.
Vacuum	27.05 in.
Size of dryer	5×30 ft.
Weight of dry rubber	2994 lbs.
Percentage of moisture removed	46.6
Steam consumption per lb. of water removed	1.14 lbs.
Steam consumption per lb. dry rubber	1.001 lbs
Power required for vacuum pump	9.43 h. p
Power required for dryer	9.50 h. p
Floor space of equipment including working space	540 sq. ft.
Cost	
2997 lbs. of steam at 40 cts. per 1000 lbs.	$1.199
10,800 gal. water at 6 cts. per 1000 gal.	0.648
66.97 k.w. hrs. at 1.5 cts. per hr.	1.005
0.8 hr. supervision at 40 cts. per hr	0.320
1.0 hrs. loading and unloading at 40 cts. per hr.	0.400
Total	3.572
Cost per lb. of dry rubber	0.001193
Cost per ton of dry rubber	2.386

---

[1] The data illustrating the expense of operating the various types of dryers do not include any interest on investment, depreciation of equipment, etc., owing to the great variation in cost of buildings, cost of erection, etc., in different localities, and in the cost of the equipment itself in recent years.

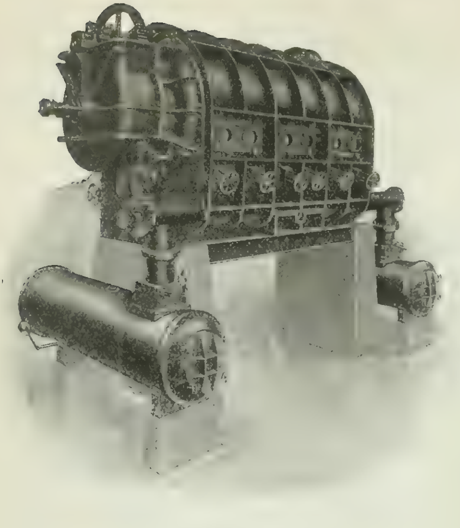


Fig. 4

Vacuum Drum Dryer

Since the vacuum drum dryer is designed for the immediate conversion of liquids into dry products, it operates upon different principles from the rotary or shelf type, and eliminates several operations otherwise necessary to separate a liquid from its solutions. A cast-iron casing encompasses a drum to which the liquid is applied, and through which the heating medium is circulated. The dryer operates under a high vacuum, which greatly reduces the boiling point of the liquid material and hastens the removal of vapors which are conducted as usual through a dust collector to a condenser.

The liquid is distributed on the revolving drum in a thin film. Film drying is exceedingly efficient and economical, for heat transmission to a liquid is much more rapid than to solids or semisolids. We have therefore in the case of the film a much higher rate of evaporation of the moisture—an evaporation which often reaches a value of 5 lbs. or more per sq. ft. of heating surface per hr. and which of course greatly exceeds that of either the shelf or rotary systems. The rapidity of evaporation from the film is related to the fact that the large area over which the film spreads on the drum facilitates the release and escape of the moisture. The process of evaporation is sufficiently rapid so that the greater part of the moisture is removed during a partial revolution of the drum, whereupon the dry material is scraped off by means of a knife placed as near as possible to the point at which the film is applied, in order that the greatest possible heating surface of the drum may be utilized. As the solid material falls from the knife it is collected in a receiver, which is usually jacketed and heated by means of low pressure steam or hot water in order to prevent water vapor collecting on its inner surface, to the detriment of the dried material. The dry product often falls into the receiver as a powder, and sometimes in the form of a ribbon which may or may not require further treatment before it is shipped. Products that are excessively sticky, or that adhere rigidly to the drum, creating a hard film which passes the knife and retards heat transmission, cannot be dried to advantage.

Where the dry material is of such a character that it can be mechanically conveyed, a continuous operation requiring a minimum of supervision is made feasible by installing two receivers which are operated alternately and which are connected to an additional small vacuum pump for evacuating the receiver just discharged and emptied before it is again united with the main drying system, the additional expense being more than offset by the increased capacity.

Since the actual drying period is exceedingly short, being less than that required for one complete revolution of the drum, this type of dryer is especially suited to the drying of those substances that are sensitive to heat, as, for example, milk, eggs, tanning and medicinal extracts, soluble coffee, tea, etc. Substances that are injured by cast iron may be dried in a copper-lined dryer equipped with a bronze drum. Attention should be called to the fact that the dryer may be operated atmospherically, and that so used it has been successful in the drying of various insecticides, glue, sodium benzenesulfonate, etc. Used atmospherically, the rate of evaporation is less, on account of a lower temperature difference, while radiation and steam consumption are high, though the actual cost of equipment is greatly reduced.

In all instances it is highly desirable, if a maximum capacity is to be attained, that the liquid to be dried be brought to as high a concentration as possible before it is introduced into the dryer.

The moisture content of the finished product is from less than 0.5 per cent up to 3 per cent, depending on the physical characteristics of the material. In the case of glue the moisture content may even run up as high as 10 to 12 per cent. It is to be noted that this moisture content can be regulated by control of steam pressure, speed of the drum, and thickness of the film.

There are various types of drum dryers, which differ principally in the method employed in applying the liquid to the drum. In the Eckenberg type liquid, on being introduced into the system, is partially concentrated by coming into contact with the end of the heating drum. The liquid then flows into a reservoir directly underneath the drum,

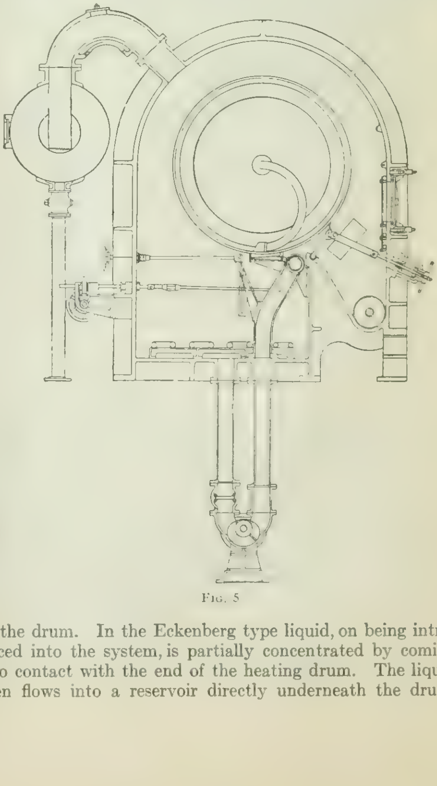


Fig. 5

which in passing through collects some of the liquid on its surface. The material which so adheres is continuously scraped off in the form of a dry ribbon.

One of the Passburg types provides that the drum dip into the liquor supply, whereas in another type the drum is not in contact with the main body of liquid, but the solution is conveyed to the drum surface from the liquor supply tank by a small roll situated parallel to and directly under the drum.

In the double drum type the liquid or semiliquid is applied between heated drums revolving in opposite directions. The solution is forced between the rolls, and the material which adheres is scraped off in the upper quarter of the revolution.

The Buflovak type utilizes a circulating device for applying the liquid. The main body of the liquid is held in a large reservoir in the bottom of the casing, from which it is continuously pumped to a pan directly below and close to the drum. A slight pressure is maintained in this pan which tends to force the liquid against the drum surface and to compel it to adhere to the drum as it passes through the pan. This method gives a uniform coating, which, combined with the control obtained by an adjustable spreader bar, makes possible an accurate regulation of the film thickness. The overflowing liquid from the pan drops back into the tank and is recirculated.

The running expense of drying sulfite waste liquor by th continuous process is as follows:

Size of drum	5×12 ft.
Steam pressure	39 lbs.
Vacuum	27.8 in.
Speed of drum	8.25 r. p. m.
Drying time	7.27 sec.
Duration of test	4 hrs.
Weight of liquor, 31.9° Bé. at 60° F.	8011.00 lbs.
Weight of dry material	4483.00 lbs.
Weight of dry material per hr.	1120.75 lbs.
Moisture in solution	47.83 per cent
Moisture in dry material	6.76 per cent
Steam consumption per lb. water evaporated	1.165 lbs.
Steam consumption per lb. dry material	0.917 lb.
H. p. of drum, pumps, and conveyor	30.16 lbs.
Supervision	1 man
Floor space of equipment including working space	797 sq. ft.

COST

4112 lbs. of steam for drying at 40 cts. per 1000 lbs.	$1.6448
4102 lbs. of steam for power at 40 cts. per 1000 lbs.	1.6408
12,700 gal. water for condenser at 6 cts. per 1000 gal.	0.7620
4 hrs. labor at 40 cts. per hr.	1.6000
TOTAL	5.6476
Cost per pound of dry material	$0.001259
Cost per ton of dry material	2.518

Using motor driven equipment the cost would be:

4112 lbs. of steam at 40 cts. per 1000 lbs.	1.6448
12,700 gal. water at 6 cts. per 1000 gal.	0.7620
90 k.w. hrs. at 1.5 cts. per k.w. hr.	1.3500
4 hrs. labor at 40 cts. per hr.	1.6000
TOTAL	5.3568
Cost per lb. of dry material	0.001195
Cost per ton of dry material	2.390

Potash from Kelp. IV—Continuous Countercurrent Lixiviation of Charred Kelp[1,2,3]

By J. W. Turrentine and Paul S. Shoaff

EXPERIMENTAL KELP POTASH PLANT, BUREAU OF SOILS, DEPARTMENT OF AGRICULTURE, SUMMERLAND, CALIFORNIA

In a chemical process involving the extraction of water-soluble constituents from solids and the recovery of the solution or of the solid residue or both, the ultimate object is the complete removal of soluble matter; and in cases in which the solution is to be processed, the coincident aim is the production of a solution as highly concentrated with respect to the solute as is practicably and economically allowable under the specific conditions.

This frequently encountered problem arose in the determination of an efficient and economical method for extracting the potash salts from charred kelp. Its solution is described in the following paragraphs.

Nearly all of the material extracted is "activated" char, which is the product of the reduction of the giant Pacific kelp, *Macrocystis pyrifera*, by a process consisting, briefly, of drying the wet kelp in direct-heat, rotary dryers, charring the dried material by destructive distillation in retorts or in other manner, and activating the charcoal by subjecting it to a special heat treatment. From the activated char are recovered potassium chloride, iodine, and decolorizing carbon. This process has been described in a general way in a previous article.

The activated char averages 75 per cent total water-soluble constituents and 52 per cent potassium chloride, and will yield an amount of decolorizing carbon depending, among other things, on the manner and degree of activation. The greater part of the water-soluble matter other than potassium chloride is sodium chloride. The manner in which the char is extracted for potash values is of interest not only in connection with the recovery of potash and by-products from kelp, but has wide adaptation in other fields, where materials are to be completely washed free from values or from impurities, and particularly where a completely extracted solid and a concentrated filtrate are desired simultaneously. The apparatus has been successfully operated for about two years, and its efficiency and low cost of operation are thoroughly established.

In the washing of a precipitate, it is recalled, one is taught that the most complete extraction of the things whose removal is sought is accomplished by transferring the precipitate from the filter to a container and stirring it thoroughly with the quantity of wash water to be used in each individual application and returning the mixture to the filter; but since this is scarcely practicable, one is taught to stir the precipitate on the filter with a stream of the wash water. To add water without stirring washes imperfectly, since the wash water merely establishes channels through the solids. For that reason, washing solids as filter cake on continuous vacuum filters removes impurities only imperfectly and, where a concentrated filtrate is desired, at a rate which may preclude the subsequent use of the washings.

In the large-scale washing of a precipitate or extraction of a solid in the lixiviator herein described, it is practicable to remove the solids from the filter and transfer to a container, there to be stirred with the water or brine being built up. This is repeated as desired, the number of washings being determined by the number of filter units comprising the lixiviator. That number may be multiplied to suit the problem in hand, the multiplication of the number of units but very slightly increasing the difficulties or expenses involved.

The system here described may properly be termed countercurrent lixiviation. The material to be leached is fed in a continuous stream into one end of the apparatus and passes out of the other end as a satisfactorily washed and largely dewatered filter cake, the while advancing against a stream of water which enters at one end as fresh water and emerges

---

[1] Received April 25, 1921.

[2] Published with the permission of the Secretary of Agriculture.

[3] Part I, by J. W. Turrentine and Paul S. Shoaff, THIS JOURNAL, 11 (1919), 864; Parts II and III, by G. C. Spencer, *Ibid.*, 12 (1920), 682, 786.

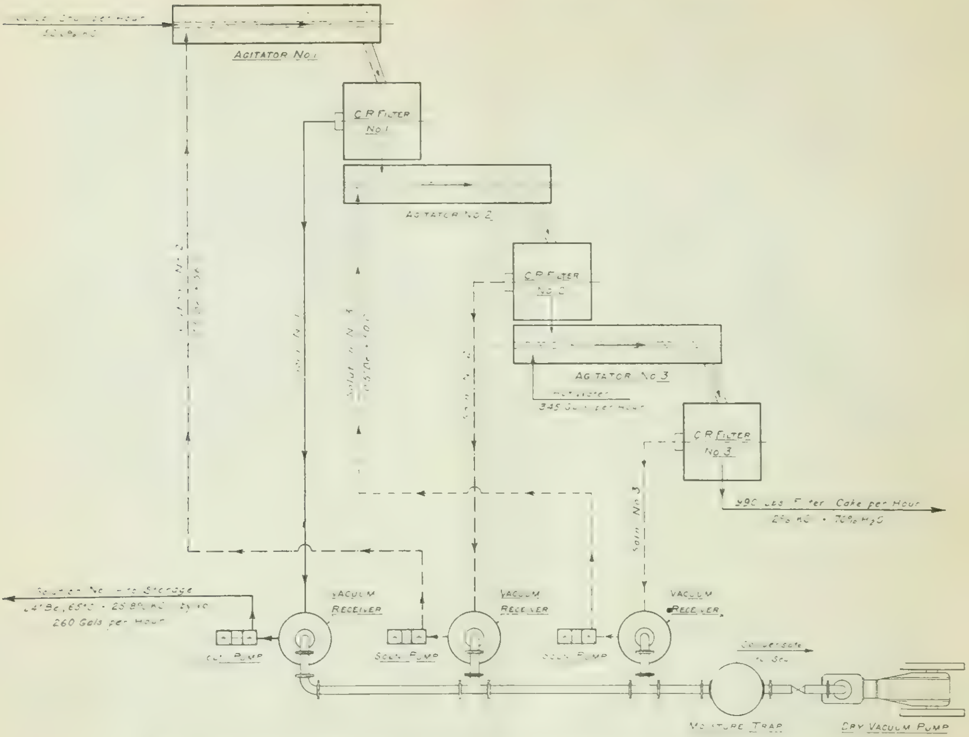


FIG. 1—FLOW SHEET OF CONTINUOUS COUNTERCURRENT LIXIVIATION OF ACTIVATED CHARRED KELP

at the other as a highly concentrated brine. This is accomplished in a lixiviator of only three units, a unit being a container wherein the solid is stirred with its quota of water, and a filter, with accessory apparatus. For materials less easily extracted, more units would be required. Each unit accordingly represents a stage in the complete extraction, and each stage represents an application of the extracting agent and a filtration.

The units comprising such a lixiviator are made up of a leaching tank, a rotary vacuum filter, with vacuum receiver, and brine pump.

DESCRIPTION OF APPARATUS

The leaching tank, which we shall hereafter designate as an agitator, is made of 2-in. redwood, 14 in. x 14 in. x 7 ft. 6 in. inside, and is of standard construction. It has a removable cover of 2-in. redwood, with suitable openings for the entrance of filter cake, brine, etc. In each tank is a 12-in. steel screw conveyor with specially constructed flights by means of which the contents are thoroughly mixed and simultaneously conveyed. The shafts of the agitating screw run out through the ends of the tanks through cast-iron stuffing boxes, and one shaft in each case is extended to run in a journal and to receive a sprocket wheel for driving. Steam heating coils are placed in the bottom of the tanks. At the discharge end of the agitator tank there is an opening on one side at the top, 3 in. deep and 4 in. wide, from which a 4-in. open trough leads to the tank of the appropriate rotary filter, the trough having a slight fall. This delivers the mixture of solid and liquid in the form of a sludge into the tank of the filter.

The continuous, rotary, vacuum filters may be any of the well-known multiple compartment types, although the one here employed is the one known as the American disk continuous suction filter. Each filter has one 4-ft. diameter disk, of an approximate filter area of 21 sq. ft. It is made up of eight removable filter-leaf segments clamped to a central shaft by rods extending radially from this shaft. The shaft is subdivided into eight longitudinal pipe compartments, each leaf segment being connected to one compartment.

On one end of the central shaft is a worm gear driving mechanism for rotating the entire disk. At the other end is an automatic distributing valve with eight ports connecting the pipe compartments of the shaft to the solution suction lines and to a back pressure air line for inflating the filter bags and discharging the cake.

The disk is mounted in a tank into which flows the sludge to be filtered. The sludge is maintained at such a level as to cover the leaf segments of the lowest section of the disk.

In operation the sludge flows continuously into the tank, and as the disk rotates, the filtering surface passes through the sludge. As each segment under vacuum is immersed, a cake begins to build and continues to build until the segment emerges above the sludge level. The liquid passes through the filter cloth and vacuum pipes to the automatic valve, while the solids adhere to the filter surface on both sides of the disk in a cake from 0.25 to 0.5 in. thick.

The segments bearing the cake enter the drying area, where the moisture content is reduced by reason of the continuous suction, and then successively move into the discharge zone comprising an arc of 15°, where the vacuum is cut off and air at 15 to 20 lbs. pressure is automatically admitted through one valve port to the segment in this zone to loosen the cake from the filter cloth. The cake is scraped off by a metallic scraper and drops into the agitator of the following unit. The disk rotates at a speed of one r. p. m.

The vacuum receiver is a steel cylinder, insulated, 16 in. in diameter by 5 ft. high. It serves to separate the air from the solution drawn over from the filter to which it is connected. As is the usual arrangement, the solution line from the filter enters on the side of the receiver, a drain line passes from the bottom to the solution pump, and the vacuum line enters at the top. The solution from each filter is drained from the receiver by an individual pump which conveys it to the proper agitator or storage tank, as the case may be. The receiver from each unit is connected to a common vacuum line running to a single vacuum pump.

The moisture trap is a steel cylinder, 16 in. diameter by 3 ft. high, with internal baffles. The condensate from water vapor or entrained solution runs to a seal and is returned to the system.

The dry vacuum pump has a capacity equivalent to a displacement of 153 cu. ft. of free air per min. at 350 revolutions. In addition to this, a low pressure air compressor is provided to furnish air at 15 lbs. per sq. in. to the automatic valves of the filters for loosening the filter cake before it reaches the scrapers. Steam may be substituted for air at any time for cleaning the filter cloths of particles tending to clog the pores.

The three units are arranged in series in echelon order, so that the filter cake from the filter of one unit falls by gravity into the agitator of the next. The brine from the filter of one unit is delivered by the appropriate pump into the agitator of the preceding one. Thus, the solids pass through the system by gravity flow, while the brine is passed through by the aid of pumps. The total fall from end to end is 28 in. The concentrated brine from the first unit is discharged by its pump into the so-called hot storage tank for strong brine, from which it is drawn off as desired into the evaporating and crystallizing system, and the filter cake from the last unit is discharged into a conveyor for transference to the carbon refining department. Fresh water is added to the last agitator. Brines of three concentrations—weak, intermediate, and strong—are received from the respective units; and solids of four degrees of extraction—the raw material and the filter cake from the respective three filters—are handled.

OPERATION

The operation of the apparatus is illustrated diagrammatically by Fig. 1, which is a flow sheet of the system.

The ground charred kelp, as a dry powder, is fed continuously into Agitator 1 and the solution or filtrate from Filter 2 is constantly delivered to the same point. The sludge resulting from this mixture of fresh char and brine, after thorough agitation, flows by gravity into the tank of Filter 1.

The solution from Filter 1 is drawn into its individual vacuum receiver from which it is pumped to storage tanks. This No. 1 solution, or "strong brine," as it is termed in the plant, is the highly concentrated solution from which potassium chloride and iodine are ultimately recovered.

The cake from Filter 1 is discharged into Agitator 2, together with the solution from Filter 3. The resulting sludge flows to Filter 2, which produces the No. 2 solution sent to the first unit, and which discharges a cake into Agitator 3. Hot fresh water flows into this last agitator with the No. 2 cake, and this final sludge is filtered in Filter 3.

The filtrate from the last filter is the No. 3 solution referred to as going to Agitator 2. The cake from the last filter, after its third extraction, contains an amount of potash approximately equal to that contained in the weak brine which it carries. Thus its potash seems to be in solution.

The normal operating conditions as indicated by the flow sheet may be summarized as follows:

Original Activated Char:	
Total water-soluble solids, per cent	75.0
KCl, per cent	52.0
Sludge from Agitator 1:	
Temperature, ° C.	94.0
Solution 1 (strong brine):	
Temperature, ° C	65.0
Gravity, ° Bé	24.0
KCl by volume (g. per cc.), per cent	25.8
Filter Cake 1:	
KCl (wet basis), per cent	20.0
Sludge from Agitator 2:	
Temperature, ° C	66.0
Solution 2:	
Temperature, ° C	56.0
Gravity, ° Bé	7.5
KCl, per cent	9.0
Filter Cake 2:	
KCl (wet basis), per cent	7.1
Sludge from Agitator 3:	
Temperature, ° C	55.0
Solution 3:	
Temperature, ° C	50.0
Gravity, ° Bé	0.5
KCl, per cent	1.4
Final Filter Cake, 3:	
Moisture, per cent	70.0
KCl (wet basis), per cent	1.2

The normal capacity and extraction efficiency may be summarized as follows:

Activated char lixiviated per hr	1100 lbs.
Equivalent KCl entering system per hr	572 lbs.
Strong brine (Solution 1) produced per hr	260 gals.
Equivalent KCl extracted per hr	560 lbs.
Final filter cake (No. 3) discharged per hr	990 lbs.
Equivalent KCl discharged per hr	12 lbs.
Average extraction efficiency, per cent	97.9

The average vacuum on the filter system is 18 in. The extraction efficiency and the capacity would be increased if the capacity of the vacuum pump were sufficient to maintain a vacuum of 22 to 25 in. on the system.

The strong brine (Solution 1) is normally at a concentration approaching the practical operating limit. The brine of 24° Bé. at 65° C. is equivalent to a slightly supersaturated solution at 15° C. If cooled to 15° C., accordingly, some potassium chloride crystallizes out, but to an extent reduced through the mutual influence of the salts in solution. However, there is a separation of potassium chloride in small amounts in storage tanks, where no inconvenience results.

A more nearly saturated solution at a higher temperature—which would represent a higher rate of extraction and likewise a reduced volume of water to be evaporated in the crystallization of potash salts—could be obtained, but it would involve the necessity of more thorough insulation and care in operation to prevent crystallization of salts in the lines and pumps and consequent plugging. The rapid increase in the solubility of potassium chloride in water with increase in temperature makes the use of hot water highly advantageous.

The average amount of fresh hot water added to the agitator of the third unit is 345 gal. per hr., which is about 630 gal. per ton of char. This is admitted at a temperature of 82° C. The drop in temperature may be prevented by the use of more heating coils in the agitators or of higher temperature steam.

The progress of the extraction is further illustrated by the curves in Fig. 2.

COST OF OPERATION

The entire apparatus is controlled by one man, who regulates the operations by observing the gravity of the solution. With a uniform feed of char the conditions are determined by the amount of fresh water allowed to enter the last unit of the system.

Since the capacity of the apparatus operating 8 hrs. is equal to the total daily output of char, the labor cost is that for one man working 8 hrs. per day.

The apparatus here in operation is the smallest that could be constructed with standard rotary filters.

Average operating costs per ton of char lixiviated are as follows:

Labor, @ $5.50 per day	$1.25
Electric power, @ $0.025 per k. w. hr.	1.62
Steam	.11
Water, 628 gal @ $0.205 per 1000 gal.	.128
Miscellaneous supplies	.53
GROSS COST PER TON	$3.638

In estimating the cost of operating larger apparatus, it should be remembered that no more labor will be required to operate a large extractor than the small one here described; that the power required will be somewhat greater; that the steam and water consumption will be proportional to the increase in capacity, and that the cost of all these items will vary with location.

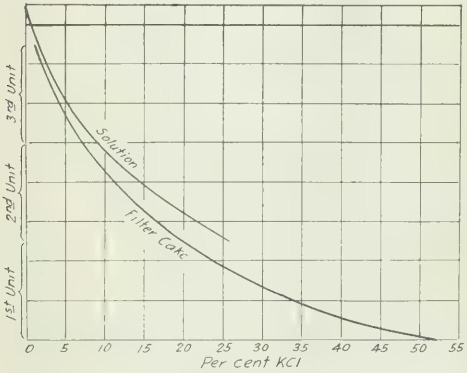


FIG 2

SUGGESTIONS FOR AN IMPROVED INSTALLATION

Experience gained in the design, installation, and operation of the initial lixiviator in use in this plant suggests modifications which might profitably be observed in its future application.

Materials of construction should be employed which will insure a long life for the apparatus. The aqueous solutions from charred kelp, although alkaline in nature, have a corrosive action upon steel; cast iron is also attacked, but less actively. Copper and brass are attacked by the ammonia in solution, and these metals in contact with iron or steel set up serious electrolytic action.

In certain instances parts of equipment may be of ordinary iron or steel as, for example, parts that are especially heavy and will function properly when somewhat corroded, or where they are not subject to erosion, or when not directly exposed to the atmosphere.

AGITATORS—The agitator tanks should be of redwood, cypress, or pine, which will last for years, and are self-insulating and easy to instal, and represent a low initial cost. A good construction is a tank that is rectangular in horizontal section, with a half-round bottom to conform with the sweep of the agitating device. They should be covered with removable wooden covers. Steam heating pipes should be run lengthwise in the tanks close to the sides. The troughs carrying the sludge from the agitators to the filters should also be made of wood.

For agitating devices, the standard cast-iron screw conveyor on which the flights are cast as paddles will serve admirably. The shaft of the screw should extend through the ends of the tank through cast-iron stuffing boxes, and should run in journals, one end extending past the journal to receive a sprocket wheel or gear for driving the device.

An agitator of the standard type with a round vertical tank and vertically hung stirring device would also be suitable, provided the arms of the stirrer could be raised when the apparatus was shut down for any length of time. Unless the latter could be done, the settlement of solids from the sludge would make starting the agitator a difficult and at times a nearly impossible matter. For gravity flow of solids, however, the height of such tanks would make this use objectionable because of the difficulty of installing the units on such widely varying levels. The horizontal agitator can be started operating at once, even after a prolonged shut-down, so that the system can be stopped "loaded" at any time and started up at will. This type also simplifies the transfer of cake from the filters.

CONTINUOUS ROTARY VACUUM FILTERS—The filters may be of the drum or disk type. If drum type, the heads should be enclosed. The tanks of the filters should be of wood, as in the usual "acid-proof" construction. Each tank should be provided with a compressed air or mechanical agitating device.

The screen on the filters should be of monel metal or wood, and if the drum type is employed, the wire winding over the cloth should be monel metal wire. The valve housings of the automatic valves may be cast iron, but the other wearing parts should be monel metal. The scrapers, likewise, should have contact edges of monel metal. Cotton filter cloth of fairly open weave is satisfactory.

On account of the free filtering nature of the sludge, each filter should have a filter area of approximately 2 sq. ft. per 100 lbs. char per hr. entering the system, with a vacuum of 22 to 25 in.

The last filter should have a spray wash sufficient to displace the most of the solution in the cake. This added amount of water will not disturb the volume balances in the system because there is a reduction in sludge volume as the char progresses through the apparatus. The filtrate and wash of the last filter should be combined.

In every case, a steam line besides the usual compressed air line should be connected to the blow-ports of the automatic valves. Air will ordinarily be used to loosen the cake just before reaching the scrapers, but it will be found advantageous at times to cut off the air and blow the cloths with steam to clear them of fine solids.

The cake from the last filter may be conveyed by a cast-iron screw running in a wooden box or by a belt conveyor. Preference will depend upon the method of final treatment of the cake.

VACUUM RECEIVERS—The vacuum receivers for separation of air from the solution drawn through the filters may be of 0.25-in. steel or heavier. They may be of the usual design employed in such systems. Cylindrical receivers 2 ft. in diameter x 5 ft. to 6 ft. high, with conical bottoms, are suitable for quite a range in filter capacities. They should have flanged connections on top, side, and bottom to the vacuum line, solution line from filter, and to solution pump, respectively. It is desirable to equip all receivers with vacuum release valves actuated by floats, to prevent solutions from being carried over into the vacuum pump in case of the failure of a solution pump to operate properly. Their elevation should be such that the solution inlets are about on a level with, or lower than the automatic valves of the filters.

All the receivers and the pipe lines carrying solutions to and from them should be well insulated.

SOLUTION PUMPS—For removing the solutions from the receivers and conveying them to their respective agitators or storage tanks, well-designed centrifugal pumps should be provided. The casings and runners of these pumps may be cast iron, but the shafts should be monel metal or steel with monel metal sleeves. Unless otherwise provided for, self-priming of the pumps should be insured by a by-pass from the impeller "eyes" to the respective vacuum receivers.

The vertical distance from the solution pumps to the receivers should be as great as possible; the nearer the distance approaches 30 ft., the simpler the pump requirements become.

A steam line should be connected to the strong brine line just beyond the outlet from Pump 1 to be used to clear the line in case of clogging with crystallized salts.

VACUUM PUMP—The vacuum on the system should be maintained by a dry vacuum pump. Its capacity should be approximately equivalent to a displacement of 4 cu. ft. of free air per min. for each sq. ft. of filter area.

COMBINED MOISTURE TRAP AND CONDENSER—Between the vacuum receivers and the vacuum pump there should be interposed a simple, vertical condenser, which will serve the double purpose of catching any entrained solution and condensing the vapors from the hot solution coming into the receivers. This will not only protect the pump, but will increase the efficiency of the vacuum system. Sea water will usually be available for the condenser. The condensate should pass through a "barometric leg" to a seal tank and be discarded.

PIPES AND VALVES—Standard galvanized pipe may be used throughout the system, though cast-iron pipe would represent an ultimate saving in certain instances. In any of the solution lines, the all-iron lubricated plug valve will give excellent service, also all-iron plug cocks of some designs and monel metal fitted valves can be used.

RELATIVE POSITION OF APPARATUS—An ideal arrangement of the different apparatus would be such that the agitators, rotary filters, and vacuum receivers would all be on one floor level; for example, on the upper floor of a 2-story building. The solution pumps should be placed on the lower floor. The combined moisture trap and condenser should be at such a height that the drain line from it to a seal tank located on the lower floor would be a "barometric leg." The dry vacuum pump would be placed in any location desired and at any convenient elevation.

EXTRACTION

The minimum amount of water or other solvent which may be used in such a lixiviator is that which will hold as a saturated solution the amount of solute to be extracted; or else the amount of solvent which, mixed with the solids to be extracted, forms a sludge which will flow from the agitator to the tank of the filter. Where the solute is slowly soluble, the time of contact with solvent may be increased by increasing the length of the agitator. To the same end, more violent agitation therein may be obtained by the simple device of increasing the speed of rotation of the agitating paddles. More complete extraction is obtainable by increasing the number of stages or units; likewise by more completely dewatering the filter cake.

OTHER APPLICATIONS

It is obvious that, where only extraction without the countercurrent feature is desired, it is necessary only to add fresh volumes of the extracting agent to each agitator and to discharge the filtrate wherever desired. This can be done without impairing the multiple stage and automatic feature of the apparatus.

The principle and apparatus here described are applicable conversely to the purification of solutions with some solid adsorbing agent, such as bleaching or decolorizing carbon. In the application of these materials, an excessive amount of the adsorbent must be used with a single application to secure a complete bleaching or purification, while much smaller quantities may be used with the same purification if the material is applied countercurrentwise.

This partially spent carbon can be induced to take up more impurities from a fresh portion of the solution to be purified; which is to say, that carbon which has lost its power to absorb impurities from a partially purified solution is still capable of taking up some impurities from an untreated solution. In such an apparatus as here described, the solution to be purified would take the place of the fresh water, and the fresh carbon, the unextracted kelp charcoal. Thus, the nearly spent carbon would be used finally to treat the crude solution entering the apparatus, and the fresh carbon, the almost completely extracted solution. The number of applications would be determined by the number of units, and time, temperature, and rate would all be easily adjusted over a wide range.

The spent carbon finally would pass from the last filter to the reactivating apparatus. A limiting feature would be encountered in the treatment of solutions whose viscosities would preclude their filtration in vacuum filters. A similar apparatus likewise may be employed in the reactivation of carbon by the wet methods.

SUMMARY

A continuous, automatic, countercurrent, multiple stage lixiviator is described, which is based on the employment of any one of the standard continuous rotary filters.

The solids to be extracted are alternately extracted and filtered. They flow through the apparatus countercurrentwise against a stream of the leaching agent. The apparatus, developed for the extraction of potash salts and other values from kelp charcoal, is applicable to the washing or extraction of any materials that can be filtered on the standard vacuum filters.

The efficiencies obtained and costs of operation are shown. Suggestions for various improvements are given.

National Research Council

Research facilities of American industries are to be described in the forthcoming revision of *Bulletin of the National Research Council*, Number 2, "Research Laboratories in Industrial Establishments of the United States of America." It is hoped that several hundred new names will appear in the revision. The demand for the first edition shows the wide interest in this subject, and the importance of having every laboratory which devotes even a portion of its time to research properly listed.

The Council requests information from directors of research who have not already supplied it. The following data are wanted: name and address of firm and address of laboratory; name of director of research; number on laboratory staff (classified as chemists, engineers, bacteriologists, etc.); approximate proportion of time spent on research; chief lines of research; unusual features of equipment; research laboratory space; date of organization of research laboratory and annual expenditure for research. Confidential information is not desired.

This material should be furnished as promptly as possible to the Research Information Service, National Research Council, 1701 Massachusetts Avenue, Washington, D. C.

The fifth annual report of the Council has recently appeared. The program laid out at the time of its reorganization from a wartime to peacetime organization in 1918–19 has so far been followed along its essential lines, the principal changes being ones of extension. During 1920 the Council has been an organization controlled by its own membership and supported by other than government aid. The Council, however, maintains close contact with government departments through its division of Federal relations.

A Study of the Fundamental Laws of Filtration Using Plant-Scale Equipment[1]

By Fred P. Baker

School of Chemical Engineering Practice, Massachusetts Institute of Technology, Cambridge, Massachusetts

There is at present to be found in the literature very little information that is of immediate value to the designer of the plant filtration unit, when he wishes to determine accurately the size of installation necessary for his purpose. The object of the present investigation was to study some of the factors determining the capacity of a filter press, using commercial-size filters, and to show the applicability of a simple fundamental equation expressing the relationship between rate of flow, pressure, and thickness of cake. It was also purposed to demonstrate the proper way to increase the pressure and also the most efficient filter cycle length. The tests were performed by students in the Graduate School of Chemical Engineering Practice of the Massachusetts Institute of Technology, as a part of the regular course, and, incidentally, they form a characteristic illustration of the training and experience the students receive. Two of the students, Messrs. A. J. Hartsook and J. Keats, were in charge of the tests and were mainly responsible for their design and performance. The work was carried out in the plant of the Revere Sugar Refinery, Charlestown, Mass., one of the coöperating companies of the School of Chemical Engineering Practice.

Discussion of Theory

From the work of various experimenters, it is safe to say that the rate of flow of liquid through a filtering medium is proportional to some power of the pressure, and inversely proportional to the thickness of cake. It is also proportional to the area of filtering surface exposed. We may express these relationships by the equation

$$R = \frac{C\,A\,P^n}{L} \tag{1}$$

where R = rate of flow of liquid
A = area of filtering surface in sq. ft.
P = pressure in lbs. per sq. in.
L = thickness of cake in in.
C = proportionality constant, depending on the nature of the sludge
n = constant, also dependent on the nature of the sludge

Now, in general, the thickness of the cake is, of course, proportional to the volume of cake, which is proportional to the total volume of liquid put through the press at any time, if the sludge is kept thoroughly agitated. Consequently, we have

$$L\,A \doteq \alpha V$$

where $L\,A$ = volume of cake
V = total volume in cu. ft. of liquid filtered at the time when the cake thickness is L
α = proportionality constant

Substituting back in Equation 1 we have

$$R = \frac{C\,A^2\,P^n}{\alpha V}.$$

Combining the two constants, C and α, and writing the rate of flow as volume per unit time the equation becomes

$$\frac{dV}{d\theta} = R = \frac{K\,A^2\,P^n}{V}.$$

It has been experimentally shown, however, that the rate of flow, R, does not in all cases vary inversely as the first power of V, although the variation is not large. However, for the general equation, we will take care of such variation by raising V to some power, m, and hence we have

$$\frac{dV}{d\theta} = \frac{K\,A^2\,P^n}{V^m} \tag{2}$$

which is the *fundamental law of filtration.* It is essentially the same equation as that proposed by W. K. Lewis[1] several years ago.

The equation may be derived directly from Poiseuilles' formula for sinuous flow through capillary tubes,

$$v = \frac{K_1\,A\,\pi r^4\,P}{8\,\mu\,L}$$

where v = velocity of flow
r = radius of capillary tubes
K_1 = number of capillaries
μ = absolute viscosity
L = length of tubes

At any given temperature μ is constant, and r is a function of the amount of compression of the cake, which, as will later be shown to be experimentally true, is a power function of the pressure. Hence we may substitute K_2 for all terms except P and L, and the equation is reduced to

$$v = \frac{K_2\,P^n}{L}$$

which corresponds to Equation 1, where K_2 includes the term A in Equation 1.

It is important to note that the value of n in our fundamental filtration equation may vary considerably, according to the nature of the solid in the sludge, although it is constant for any particular sludge. We may understand this by a consideration of the cake that is deposited. According to the capillary conception of the flow of the liquid through the cake, there are innumerable small openings, corresponding to capillary tubes running through the cake. Now according to Poiseuilles' formula, the rate of flow is proportional to the *fourth* power of the radius of these capillary voids. Consequently, any change in the size of these voids must tremendously affect the rate of flow. Therefore, if we have a suspended solid of such a nature that its particles will be squeezed together to the extent of lessening the size of the capillaries by increasing the pressure of the filter, it is obvious that the rate of flow will not increase directly proportionally to the pressure. An example of this type of precipitate is ferric hydroxide. On the other hand, if we have a precipitate of the nature of sand, that is, of a very coarse, granular character, the size of the capillaries is not lessened by increase in pressure, and the rate of flow will increase proportionally to the pressure.

Previous experimental work illustrates this point very clearly. Lewis and Almy,[2] using a chromium hydroxide sludge, which is noncrystalline and easily compressed, found that the rate varied approximately as the fourth root of the pressure. In other words, the value of n, the exponent of the pressure, they found to be 0.27.

Sperry,[3] using a suspension of kieselguhr in water, found that the rate varied directly as the pressure, thus showing that, for a noncompressible solid, the value of n is 1.0. In the formula which Sperry derives, he takes the exponent of the pressure to be 1.0 in all cases, which, as proved by Lewis

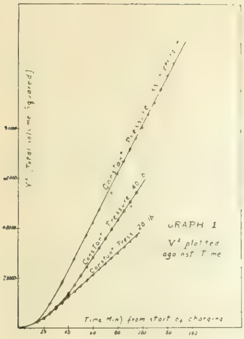
---

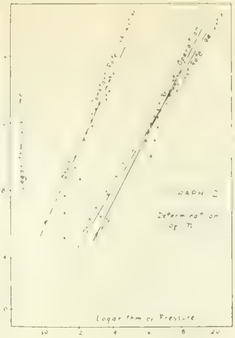
[1] Received April 4, 1921.

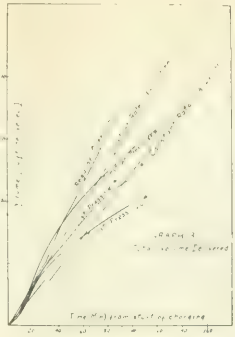
[1] This Journal, **4** (1912), 528.

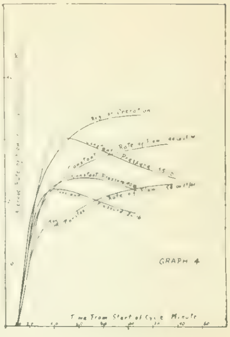
[2] *Ibid.*

[3] *Chem. Met. Eng.*, **19** (1916), 198.









and Almy, and by the results described in this article, is entirely erroneous.

The value of *m*, the exponent of the volume of filtrate, is undoubtedly somewhere in the neighborhood of 1.0. Lewis and Almy found it to be 0.81 for their chromium hydroxide sludge, and it is probable that the limit of variation is from 0.8 to 1.2.

In order to study the application of Equation 2, we have two types of flow to consider, namely: (1) constant pressure throughout the filtering cycle; (2) constant rate of flow throughout the filtering cycle.

In the first case, with pressure constant, Equation 2 becomes

$$\frac{dV}{d\theta} = \frac{K_1 A^2}{V^m}.$$

On any particular press, A is constant, and hence

$$V^m \, dV = K_2 \, d\theta.$$

Integrating

$$\frac{V^{(m+1)}}{(m+1)} = K_2\theta + \text{constant} \qquad (3)$$

the constant of integration drops out since when $\theta = 0$,

$$V = 0.$$

Now we have a means of determining whether *m* is equal to 1.0, since if

$$m = 1$$
$$V^2 = K_3\theta \qquad (4)$$

Let $y = V^2$ and $x = \theta$, then Equation 4 is $y = Kx$, which is the equation for a straight line.

Consequently, if we plot V² against 0, and the resulting curve is a straight line, Equation 4 is true, and $m = 1$. This must be so, since if *m* were not equal to unity, but equal, let us say, to 2, then Equation 4 would rightly be

$$V^3 = K_3\theta,$$

and if we plotted V² against θ for such an equation it would not result in a straight line.

In the second type of flow, namely, constant rate of flow, Equation 2 becomes

$$\frac{dV}{d\theta} = \text{constant} = \frac{K A^2 P^n}{V^{m-}} \text{ or } V^m = K_4 P^{n\theta}. \qquad (5)$$

Therefore, from Equation 5 we have a means of determining *n*, because

$$m \log V = \log K_4 + n \log P \qquad (6)$$

and by plotting log V against log P for runs made at constant rate of flow, the slope of the resulting log curve is $\frac{n}{m}$ and knowing *m*, we find *n*.

Experimental Work

In the experiments herein described, the application of the filter equation to the filtering of defecated sugar solutions by means of standard Sweetland filter presses was studied. The sludge used was that obtained by the coagulation of albumins, gums, and other organic matter by addition of lime, and by boiling the resulting solution. Kieselguhr is added to the sludge in order to form a lattice work base on the filter cloth, which makes the cake porous. If kieselguhr were not added, the slimy precipitate would almost immediately clog up the pores of the filter cloth and prevent filtration.

A copper triangular weir was constructed and placed on the outlet of one of the presses, by means of which the rate of flow of the press was accurately determined. A pressure gage was placed on the inlet of the press, and the pressure or the rate of flow, as the case might be, was regulated at will by a hand valve between the press and the pump. The latter was of the centrifugal type delivering at a maximum of about 70 lbs. per sq. in. pressure.

The tests were made on the press while it was operating on the regular plant schedule, the only change being in the variation of the pressures and rate of flow as needed. The regular cycle of operation is to filter the juice for 1.5 hrs., then sluice the cake off with the water sluice without opening the clam-shell, and repeat. The clam-shell is opened once every 8 hrs. for thorough cleansing of the cloths. In these experiments the 1.5-hr. cycle was taken for the testing period. Readings of temperature, specific gravity, rate, and pressure were made every 5 min. during the test.

For purposes of comparison, one test was made on the press operating exactly under normal plant control, that is, allowing the plant operator to change the pressure and rate of flow as he normally does. This run is described on the graphs as "Regular Operation." It was essentially a constant rate of flow run, as is shown on Graph 3, the volume-time curve being approximately a straight line.

Graph 1 shows the result of plotting V² against the time for several runs made at constant pressures, ranging from 20 lbs. to 62 lbs. These graphs are all straight lines after a few minutes at the start, during which time the cake has not formed sufficiently to give uniform filtering conditions. As shown in Equation 4, the fact that the square of the volume of liquid does vary as the first power of the time shows that the exponent *m* of the volume V in the filter equation must be equal, or very nearly equal, to 1.0 for this particular sludge.

Graph 2 shows the method of determining *n*, the exponent of the pressure term in Equation 2. From Equation 5 it was shown that, for runs made at constant rate of flow, log V could be plotted against log P, and the slope of the line would be

$\frac{n}{m}$. Since we have found that $m = 1.0$ for this sludge at least, the slope of the line must be equal to n. For the three runs that are plotted on Graph 2 the values of n are found to be 1.7, 2.1, and 2.3, giving an average value of 2.0.

At first thought this value of $n = 2$ appears entirely inexplicable. It means that the rate of flow of liquid through the filter was proportional to the square of the pressure, and it would seem that the rate could not increase more than directly proportional to the pressure, because of Poiseuilles' formula, in which the rate varies directly as the pressure. However, a reasonable explanation can be made of such a value of n by a consideration of the nature of the filter cake. It will be remembered that the sludge contained a very slimy, gummy precipitate, which was mixed with kieselguhr to aid filtration. Now kieselguhr is a substance which is very porous, the microscope revealing a structure similar to coke. We may conceive of the filter cake as built up first of a lattice work of grains of kieselguhr. Then at low pressure the slimy organic precipitate tends to fill up the space *between* these grains of kieselguhr, as filtration proceeds. But as the pressure increases, there is a tendency to force this slimy precipitate *into* the pores of the kieselguhr, thereby failing to fill up the voids between the grains of kieselguhr as fast as though the base was of a nonporous nature, such as grains of sand. This would allow more free space for the liquid to flow through than was afforded at lower pressure, and hence the rate would be increased more than in direct proportion to the pressure. It is, of course, obvious that this result will be obtained only when *two* solids are in suspension, one of which will be of a porous nature, such as kieselguhr. Any single solid in a sludge will give a value of n which is less than unity.

Since we have now determined n and m in the equation

$$\frac{dV}{d\theta} = \frac{KA^2P^n}{V^m}$$

it is possible to calculate K from the data for rates, pressures, and volumes of filtrate, since we know the area of the filtering surface.

Use of the Filtration Equation

Obviously, these values of K, m, and n apply only to this one sludge, precipitated under particular conditions, and of a definite specific gravity and temperature. Hence the numerical values of the constants are of importance at present only to the user of such a sludge. It is easy to see, however, the great value of an extensive accumulation of data on these constants from which comparative estimation of the values of K, m, and n can be made for any particular sludge under consideration.

As noted by Lewis and Almy, the real importance of the filtration equation is in affording a means of determining the area of filtering surface required for any definite amount of sludge for which the constants are known. The constants can be determined on a small laboratory filter press, and from them the size of installation required for the plant can be calculated.

For example, let us say we have made runs on a laboratory press for the sludge to be used. We have determined the constants K, m, and n for the sludge at the temperature to be used in the plant, and we have found the filter area necessary on the small press to give us a certain rate of flow—in cu. ft. per hr. Now if we know the amount of sludge to be handled in the plant, and the allowable time for filtration, we can at once calculate the area of filter surface by substituting in the filter equation the proper rate of flow, and solving for the area.

CONSTANT RATE OF FLOW SUPERIOR TO CONSTANT PRESSURE—It was also proposed to demonstrate whether it is better to increase the pressure on a filter press to its maximum at the beginning of a run, and hold it constant, or to run a constant rate of flow, which means increasing the pressure gradually throughout the filtering time. We have plotted two sets of curves which demonstrate clearly the superiority of a constant rate of flow over constant pressure when there is a compressible solid in the sludge.

Graph 3 shows, for several runs, total volume delivered at any time. It is seen that the "constant rate of flow" curves pass the constant pressure curves, and toward the end of the cycle the volume of filtrate delivered is very markedly greater.

Graph 4 demonstrates in a different manner the same superiority of constant rate of flow. Here we have plotted the average rate of flow at any time, t, against t. This time is the time from the beginning of sluicing of the previous cake. This sluicing time has been estimated at 10 min. The average rate of flow is the total volume filtered at time t divided by t, where t is again measured from the beginning of sluicing. This curve indicates the proper length of time for the filtering cycle. On such a press as the Sweetland, the point of maximum average rate of flow is not the point to sluice the press. The decrease in rate of flow as the maximum is passed must be balanced against the labor of sluicing and the extra amount of wash water to be handled. Consequently, the point at which filtration should be stopped will be somewhat to the right of the maximum on the curve. However, Graph 4 shows conclusively the advantage of constant rate of flow, as the constant pressure curves reach their maximum very early in the cycle, and then fall off rapidly, while the constant rate of flow curves have not yet reached their maximum.

These results are most conclusive in showing that the pressure should be increased gradually, and not immediately raised to its maximum, in the filtration of compressible solids. Initial high pressure forces the precipitate into the pores of the filter cloth and forms a layer through which it is very hard to force the liquid. This does not apply to noncompressible solids, such as sand, where the pressure can be increased at will, up to the limit of the filter cloth.

Further research work is at present being carried out by the Massachusetts Institute of Technology School of Chemical Engineering Practice of the study of the laws of filtration suggested by these tests, and other articles will be published in the future as the work is completed.

Summary

Commercial scale tests are described on the filtration of defecated sugar solutions.

The fundamental filter equation

$$\frac{dV}{d\theta} = \frac{KA^2P^n}{V^m}$$

as proposed by W. K. Lewis, is studied, and values of n and m are determined for one sludge. The application of the equation to the design of industrial filter installations is discussed.

Constant rate of flow is shown by tests to be markedly superior to constant pressure for filtration of compressible solids.

Acknowledgment

Acknowledgment is made to Dr. W. K. Lewis for the filtration equation used in this study, and also to Messrs. A. J. Hartsook and J. Keats for the performance of the tests and the working up of the resulting data.

The Forest Products Laboratory, in a recent "Technical Note," discusses the cause of glue stains on wood and suggests means of diminishing this effect. Such stains can be almost entirely removed with an oxalic acid solution, and still better results are sometimes obtained by using a sodium sulfite solution first.

The Thermal Decomposition of Shales. I—Heat Effects[1,2]

By Ralph H. McKee and E. E. Lyder

Department of Chemical Engineering, Columbia University, New York, N. Y.

The methods of recovering oil from oil shales are discussed in so many recent articles that they need not be repeated here. Suffice it to say that, at present, the only known methods involve the principle of destructive distillation.[1,2,3,*] This being the case, some of the factors involved in the thermal decomposition of shale have been studied. The results of this research will be published in two papers. The present one deals with the manner in which the shale decomposes under the influence of heat, while the subsequent article describes a method for the determination of the heat of reaction involved when the organic material of the shale decomposes to form oil.

Origin of Oil Shales

DEFINITION—Oil shale is defined[4] as an argillaceous or shaley deposit from which petroleum may be obtained by distillation but not by trituration or treatment with solvents. The term is also applied to those shaley deposits which are saturated with asphalt or petroleum and from which the bituminous matter can be removed by such solvents as carbon bisulfide and benzene, but the term, as ordinarily understood and in the sense in which it is used throughout this paper, excludes the oil-bearing shales and applies only to those which contain little or no bitumen soluble in the ordinary organic solvents.

The chemical composition of the oil-forming materials from which the oil is produced is little understood. Professor Crum Brown has given the name "kerogen" to the material in Scottish shale which, on destructive distillation, yields oil.[4] He defines it as neither petroleum nor bitumen, but a substance yielding petroleum and ammonium compounds on distillation.

NOMENCLATURE—Some confusion is apt to arise as a result of the designations of the various products formed one from the other. A bitumen is usually defined as a natural or pyrogenous hydrocarbon which may or may not contain oxygen, nitrogen, or sulfur, and which is largely soluble in carbon bisulfide. Abraham[5] calls the insoluble compounds, such as are found in shales, pyrobitumens. Engler[6] classifies as bitumens the whole series of products which are formed from the decomposition of vegetable or animal fats, waxes, or residues. This latter definition would include the insoluble substances, such as kerogen and pyrobitumens, as well as the soluble ones. Since the terms "kerogen" and "pyrobitumen" have been used to designate the insoluble substance, the word "bitumen" in this paper will be restricted to the soluble hydrocarbons.

INSPISSATED PETROLEUM—Little is known as to the origin or nature of kerogen or other organic material in the shale. That all of the organic or carbonaceous matter does not produce oil is known.[7] E. H. Cunningham-Craig attributes the origin of kerogen to inspissated or dried-up petroleum. He concludes that the oil shale stratum is a former oil-bearing formation which, under the action of heat, has evaporated and dried up, leaving petroleum residues which have become insoluble by polymerization.[4] Other authorities are not inclined to accept this theory, as they see no substantial evidence of petroleum having passed through the formation.

RESIN THEORY—H. R. J. Conacher,[8] on the basis of microscopic examination, describes the organic matter in the shale as (1) carbonaceous bits of plants with occasional small spores, (2) yellow bodies believed to be algae, spores, or oil globules, (3) shells of minute crustaceans, and bones, teeth, and scales of fish, and (4) sand grains. Shale portions rich in animal remains give small yields of oil. Those rich in vegetable remains give a greater yield of oil. The yellow bodies in the foregoing tests are considered vegetable matter. New Brunswick, Colorado, and Utah shales do not contain many of these yellow bodies. They are thought to be fragments of resins set free by decay and oxidation of materials of which they were once a part. Solubility of resins decreases with age; therefore the theory that failure to extract them by solvents proves that these bodies are not resins is of no value. Resinous materials from coal yield on oxidation the same products as obtained from torbanites.

Jones and Wheeler[9] report that by extraction of common coal with pyridine and reëxtraction of this extract with chloroform, coal can be resolved into cellulosic and resinic parts. On distillation of the former they obtained phenols, while the latter gave paraffins, olefines, and naphthenes.

ANOTHER THEORY—D. R. Stuart[10] is inclined to think that the kerogen may come from different kinds of organic matter, either animal or vegetable, by the action of microbes under special conditions, the product depending upon the microbe and the starting material. The kerogen, on the other hand, may be the remains of certain kinds of vegetable matter, like pine pollen or lycopod spores. He actually prepared oils very similar in properties to shale oil by the distillation of a mixture of 75 per cent fuller's earth and 25 per cent lycopodium spore dust.

ORGANIC REMAINS—Engler[11] chooses to fit the origin of the pyrobitumens of shales into the whole scheme of bitumen and petroleum formation from organic remains, successive polymerization and decomposition playing a very important part both in the character of the petroleum and in the bitumen formed.

By the decay of fats, waxes, and other animal and plant remains there are produced free fatty acids, wax esters, and hydrocarbons of the type of adipocere, montan waxes, and, perhaps, ozokerite. These are soluble in benzene, carbon bisulfide, etc. Part of this material may condense and polymerize to form what Engler chooses to call polybitumens. These are infusible and insoluble, and are found in nature as the insoluble part of the Scottish, Austrian, and Autun shales. These, under the action of heat, may go over to soluble bitumens, small amounts of which are always found in the shale, and which may also be found in nature as malthas, etc. Disintegrating further under the action of heat and pressure, these compounds go over to natural petroleum as we find it in wells, and this, on polymerization, yields the heavy asphalts.

Classification

Shales differ considerably among themselves. Upon destructive distillation, they yield products differing in character even though they be produced under similar conditions. It is estimated that Elko Nevada shales will produce paraffin wax to the weight of 35 per cent of the total oil recovered, whereas the New Brunswick shale oil contains but little paraffin. The oil from the latter resembles California crude. An attempt to classify the various hydrocarbons in these shales leads to some confusion, but a partial

---

[1] Received April 4, 1921.

[2] A dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York, N. Y.

* Numbers refer to bibliography at the end of the paper.

classification on the basis of solubility in organic solvents and chemical composition is possible.

The pyrobitumens, which form bitumens on heating, may be further subdivided into one class which contains little or no oxygen and another which does contain oxygen. Those in the first class are called asphaltic pyrobitumens because they resemble asphalts, which contain but little oxygen. They are infusible and insoluble, and include elaterite, wurtzellite, albertite, imposinite, and asphaltic pyrobituminous shales. The New Brunswick, Nova Scotia, and Quebec shales are of this type.

The nonasphaltic pyrobitumens are those which contain oxygen and oxygenated bodies, but are also insoluble and infusible. Into this class fall cannel coals, lignites, torbanites, and shales containing torbanite material. The Scottish shale belongs in this category.

DISTRIBUTION

Oil shales occur in various parts of the world in apparently unlimited quantities. In Scotland the shale oil industry dates back to 1850.[12] France began to develop shales in Autun even before the Scottish industry existed. New Zealand has several times attempted to use them.[13] In Australia several large deposits and some very rich shales occur.[14] In Tasmania there are extensive deposits.[14] In Africa there are shales in the Transvaal and in Portugese East Africa.[15] Spain and Serbia also have oil shales.[13] In the western hemisphere they are to be found in various parts of South America,[13] in Canada,[16, 17, 18] and in the United States.[19] None of these enormous deposits, except the Scottish oil shales, have, as yet, been worked with complete success.

The oil shales of the United States rival in quantity the known coal deposits. There is sufficient oil obtainable from the shales of Colorado, Wyoming, and Utah to supply the United States for several generations.[20] Colorado alone has enough shale to produce 58,000,000,000 barrels of oil.[21] When it is remembered that less than 8,000,000,000 barrels of oil have been taken from wells in this country since the first well was drilled in 1859, the quantity of oil available from these shales begins to be appreciated.

Although attention is, at present, centered on the oil shales of Colorado, Utah, Wyoming, and Nevada, it is only because these are exceptionally rich in oil-forming material. Other deposits exist,[22] and as methods are perfected for working shales the poorer ones will, no doubt, be utilized. In Kentucky there are quite extensive shale beds which, though not quite so rich as the Colorado shales, yield more oil than those being worked in Scotland at present.

The enormous quantities of shale available for oil production is the factor that continually encourages investigation in the face of all the difficulties surrounding the problem.

THE PETROLEUM SITUATION

In view of present-day statistics it must be admitted that the future of petroleum in the United States is not encouraging. The figures for 1920 show that some 110,000,000 barrels of oil were imported to make up the deficit in home production. Fig. 1 illustrates the situation as it stands.

While as yet the maximum production of petroleum in this country has not been reached, it will be seen that the consumption is much greater than the production, and the consumption is expected to increase. It was in 1895 that the first commercially practical automobile was demonstrated, and at the beginning of 1920 there were 8,000,000 automobiles, 1,000,000 trucks, and 300,000 tractors in use. Further, it is expected that by the end of 1921 there will be 9,000,000 automobiles and trucks, and 450,000 tractors in use. Aerial navigation is yet ahead, but may be expected soon to consume large quantities of particularly high-grade motor spirit.

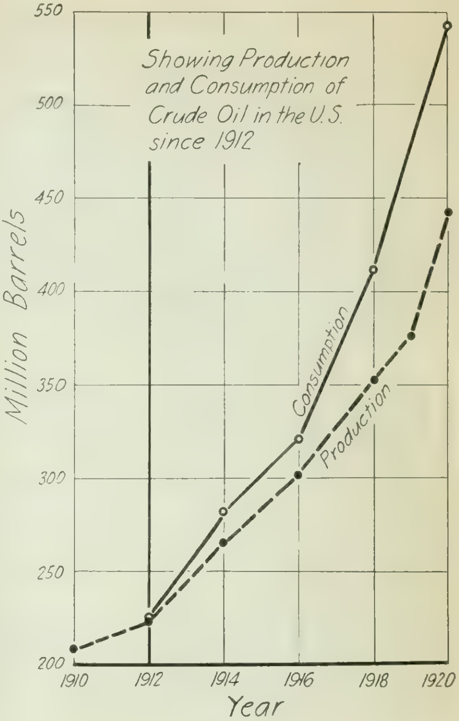


FIG. 1

That oil shale can be utilized to make up the deficiency caused by the increased consumption of petroleum is the opinion of our best authorities on the subject. In this connection we may quote Dr. Dean E. Winchester,[23] formerly of the U. S. Geological Survey:

> After spending nearly five years in studying the oil shales of the western part of the United States, I am thoroughly convinced that the day is not far distant when these very shales that the cattlemen and farmers of the Rocky Mountain region have sworn at so often because they make neither good farm land nor good range, will yield oil in sufficient amounts to prevent the rapid decline on our total production which is imminent if no new source of petroleum is developed. There seems to be every indication that in the near future (perhaps ten years) there will be established in Colorado and Utah an industry for mining and distilling of oil shales which will rival in size any mining or manufacturing industry in the United States.

FIELD OBSERVATION

An inspection trip to the Colorado, Utah, and Nevada districts during the summer of 1920 revealed the fact that considerable work of a certain nature is being done toward the development of these shales. Several retorts have been built in the field, but none of them are operating in any regular way. Some are small one-unit plants operated for demonstration and experimental purposes only. Some of the schemes will probably never work and are intended more for promoting purposes and the sale of stock than for actual production of oil. Others are making every effort to produce a retort which will successfully distil these shales. Almost all of the development seems to be toward the perfecting of a retort which will produce oil, without consideration of the character and quality of the oil produced. None of the oil is, as yet, being refined, and when refining operations are begun it is quite probable that the oil will be found deficient in quality, and some of the retorts that are furthest advanced, at present, may have to be redesigned completely to meet the necessity of producing a marketable oil. Let it be said that this does not apply to all of the plants in the field. Some are studying all of the conditions, each one in its proper relation to the other, and are making definite progress.

Thermal Decomposition of Shales

Oil shales are but little soluble in organic solvents, as has been pointed out. They are not, therefore, hydrocarbons of the type of gilsonite,[24] grahamite,[24] ozokerite,[24] or asphalt. Shales must be distilled to recover the oil and ammonia products from them. The oil is said to come from a specific pyrobituminous material, and not from the entire organic remains in the shale. From Scottish shale, oil is said to come from kerogen. In any case, upon destructive distillation of a number of different kinds of pyrobituminous substances, hydrocarbons of the nature of paraffins, olefines, and aromatics are produced.[7, 25]

The hydrocarbons, when distilled off and fractionated, yield low-boiling, intermediate, and high-boiling fractions, just as do naturally occurring petroleums. Many retorts have been designed to distil these shales, and each is based on the designer's conception of the manner in which the shales decompose. For the most part the idea seems to be prevalent that, upon breaking down, the kerogen or other pyrobitumens yield, directly, petroleum oils. Many think that they yield, first, gasoline-like products; second, heavier products, such as kerosene; next, gas oil; and so on as the temperature increases. Others believe they yield a wide range of products directly, that is to say, each molecule of kerogen will decompose into gasoline, kerosene, etc., in essentially one step. In this case the gravity of the oil should not appreciably increase as the temperature rises. It has been demonstrated in this work that neither of the above conceptions is correct. The first product of decomposition was found to be a heavy semisolid or solid bitumen which is soluble in benzene and carbon bisulfide, and it was found that the formation of the petroleum oil is a result of the cracking of this heavy bitumen. This is in accord with Engler's deduction[26] that certain pyrobitumens, when heated to certain temperatures, become soluble in organic solvents. Table I shows some of the results of the decomposition of materials of this nature.[27]

Table I—Increase in Solubility of Shale upon Heating

Source	Soluble in Benzene Before Heating Per cent	Temp. °C.	Duration	After Heating Additional Per cent	
Posidonomya shale from Reutlingen	0.6	250	24 hrs.	0.34	3.58
		300	Additional 24 hrs.	3.24	
		400	Additional 24 hrs.	0.00	
Menilite shale from Strzytki, Egst. Glacia	0.85	300	0.5 hr.	1.21	2.31
		350	Additional 24 hrs.	0.70	2.06
		350	Additional 24 hrs.	0.40	
Shale from N. S. Wales, Australia	1.40	250	2 days	1.33	
		250	Additional 8 days	0.73	
Shale from N. S. Wales, Australia	1.40	300	2 days	28.50	36.3
		300	Additional 8 days	7.80	
Shale from N. S. Wales, Australia	1.40	400	1 hr.	4.90	55.2
		400	Additional 2 hrs.	44.90	
		400	Additional 2 hrs.	5.40	
		400	Additional 2 hrs.	0.00	

If this deduction is correct it is of considerable importance, and if proved experimentally would define methods for shale distillation superior to the ones now used. Experimental work was carried out as follows:

Experimental methods—The finely ground shale, 60-mesh, was placed in a 2-in. iron tube, 20 in. long. The tube was capped at both ends and fitted with a pressure gage. The whole was placed in a rotary-type, gas-heated furnace in which it was possible to control the temperature very accurately. A base-metal thermocouple was also placed in the tube with the shale. The shale was heated in this apparatus for periods of time ranging from 1 to 8 hrs. It was then taken out and examined, and the amount of soluble material in it was determined. Observations were made on the temperature and pressure as the heating progressed.

It was found that in some cases when the shale was heated for 6 hrs. around 390° C., no apparent change occurred. Little gas was given off, as was indicated by the fact that the pressure remained around 25 or 30 lbs. per sq. in. Slight increase in solubility was noted, but the shale in general maintained its hard, rubber-like texture. In other experiments only a few degrees higher (394° to 398°), and in one case at the same temperature, decided changes were noted. The pressure suddenly rose after the shale became heated up, and remained around 100 lbs. per sq. in. The product was a black tar-like mass with the shale residue suspended in it. Upon extraction with benzene this yielded 30 to 40 per cent of soluble material, as compared to 1.5 to 2.9 per cent on the original shale.

It was not possible in these experiments to keep the tubes entirely tight, and some gas and vapors usually escaped. This rendered the results inconclusive. Although a heavy product was obtained, as was expected, it could easily have been the result of the light vapors having been lost by distillation, but the results did show that a decided change was taking place in the shale, and this at a quite definite temperature.

The pyrometer used in these determinations was of the ordinary base-metal type and was, unfortunately, equipped with a relatively low resistance indicator, which rendered the results somewhat questionable. On this account other means of studying the changes that were taking place were adopted.

The final method was to distil the finely pulverized shale under atmospheric pressure in a small, electrically heated, brass retort, shown in Fig. 2. This apparatus had the advantage that the temperature could be controlled accurately and could be measured to within the experimental error of the mercury thermometer. Also, it was desirable that the distillation be made under atmospheric pressure.

The run was made as follows: About 25 g. of shale were placed in the retort. After the temperature of the metal bath had reached that at which it was desired to make the run, the retort was set in place and allowed to heat for 1 hr. 20 min. The temperature was measured by means of a 500° C. nitrogen-filled mercury thermometer placed in the bath. In one run thermometers were placed both in the retort and in the metal bath in order to determine the temperature lag through the shale. It was found that the center of the retort attained the temperature of the bath within 20 min.; hence, in order that all the shale might stay at the desired temperature for an hour, the heating was continued for 1 hr. 20 min. Preliminary tests had shown that if the shale did not decompose at a given temperature within an hour it could be heated at that same temperature for several hours with no apparent change. During the determination the thermometer was not used in the retort, as shown in the figure, but was placed directly in the bath. It was only the highest temperature that was of interest and, of course, this could be more easily obtained in the bath than elsewhere. The oil that distilled over was caught and measured.

After the shale had been heated for 1 hr. it was removed from the retort and extracted in a Soxhlet extractor with carbon bisulfide to remove the heavy oil or bitumen which had formed but had not distilled over. This bitumen was

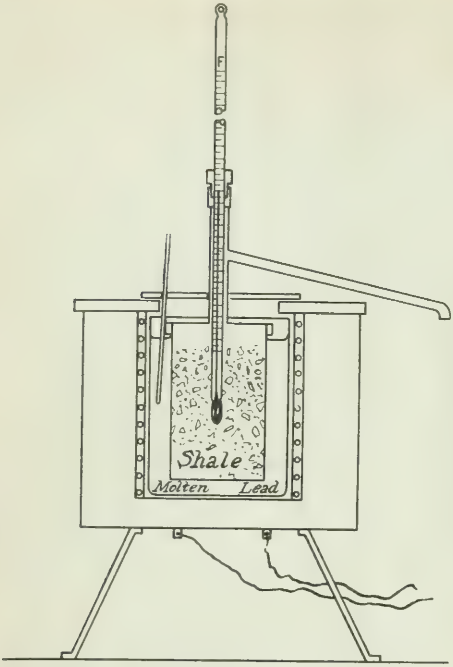


Fig. 2

freed from carbon bisulfide by evaporation, and weighed. Several runs were made, varying the temperature by small increments each time.

DETERMINATIONS—The shale used was from the Parachute Creek district near Grand Valley, Colorado. It had the following properties.

Massive Type Shale	
Specific gravity	1.60
Specific heat	0.25
Moisture, per cent	0.13
Volatile matter, per cent	53.90
Ash, per cent	47.00
Oil yield per ton, gal	63.50
Solubility in CS_2, per cent	1.96

Run 1—This run was made as described above, with the bath kept at from 373° to 375° C. Eighty-five hundredths of a gram of oil distilled over and 1.45 g. of heavy bitumen were extracted from the residue. The shale was but slightly changed in appearance, and had not lost its hard massive texture.

Run 2—This run on 24 g. was like the previous one, except that the temperature was kept at 384° to 386° C. One and three-tenths grams of light oil were obtained, with 1.52 g. of heavy bitumen. Little change was seen in the general appearance of the shale; it was, however, slightly darker.

Run 3—This run was made at 398° to 400° C. One and seventenths grams of light oil were collected and 1.9 g. of bitumen. No noticeable difference had occurred in the appearance of the shale.

Run 4—A run at 425° C. yielded 4.2 g. of light oil and 4.93 g. of heavy bitumen. The character of the residue was decidedly changed. It was a dry coke-like mass which could be easily pulverized with the fingers to an impalpable powder, the original hardness and general character of the shale having been entirely destroyed. The specific gravity of the bitumen recovered was about 1.

Run 5—This decided change within 25° suggested that valuable information might be gained by taking an intermediate step. In a run made at 410° C., the amount of light oil was 2.55 g., and the amount of bitumen was 6.4 g. This bitumen, when extracted and dried, was of a rather rubber-like texture. The residue left in the retort before extraction was not a dried coke mass as in Run 4, but a sticky, tarry conglomeration which held together quite tenaciously. The following are the tabulated results of the five runs:

	Temp.	Light Oil		Heavy Oil (Bitumen)		Total Oil	
Run	° C.	G.	Per cent	G.	Per cent	G.	Per cent
1	374	0.85	3.4	1.45	5.7	2.30	9.1
2	385	1.30	5.3	1.52	6.2	2.82	11.5
3	399	1.70	7.0	1.90	7.9	3.80	14.9
4	425	4.20	16.8	4.93	19.6	9.13	36.4
5	410	2.55	10.2	6.40	25.6	8.50	35.8

No correction has been made in these figures for the original 1.96 per cent soluble in carbon bisulfide before heating. The figures would, of course, bear the same relation to each other as is shown above. Fig. 3 is the graph of these various factors.

INTERPRETATION OF RESULTS—The interpretation of the results of the experiments just described is plain and important. As the temperature rises in each successive determination, increasing amounts of oil are produced, but the quantity is rather small. At between 400° and 410° C. the curve suddenly rises, showing a complete destruction of the insoluble kerogen bodies in the shale. The temperature limits are seen to be close. This would indicate that the kerogen has a decomposition temperature which is definite to within 10° C.

Although it is seen from the curves that light oil is always produced, more of the heavy bitumen than light oil is produced at the lower temperatures. At the temperature of decomposition, *i. e.*, where the curve starts abruptly upward, by far the largest part is heavy bitumen, and during decomposition large quantities of heavy oil are produced, with no corresponding increase in light oil. If light oil had been directly produced from the kerogen, its curve would have followed the heavy bitumen curve.

Cracking of Shale Oils

Another item of importance in connection with these decompositions is that the shales decompose at temperatures above the point where cracking will take place to a limited extent. It is seen that even at 375° C., where the decomposition of the kerogen was relatively slow, some light oil was formed, but cracking became rapid at almost the same temperature as that at which the shale decomposes.

The break and descent of the bitumen curve with no change in the total quantity of oil show conclusively that the heavy bitumen is decomposing to form light oils.

Another important point is noted here. Various distillations of this Colorado shale, either in 2-lb. lots or 20-lb. charges, under the most careful conditions, yielded 63 gal. of oil per ton. The oil obtained had a specific gravity of 0.921, which means 480 lbs. of oil. Add to this 20 lbs. of gas obtained, and we have 500 lbs., or 25 per cent of product per ton of shale. The amount of product obtained when the shale was heated just to its decomposition temperature was 36 per cent, or 720 lbs. per ton. If all this could be converted into oil of 0.921 specific gravity, it would yield 91.5 gal. of oil per ton. There would, of course, be a cracking loss if the tar were converted into light oils after its removal by solvents. This calculation is included to show that the maximum hydrocarbon yield is not produced by the present method of distillation and that it is the phenomenon of cracking that produces the light oils with which the industry is familiar

These deductions place shale oil on the same basis as cracked products from naturally occurring petroleum. It has been shown that little or no gasoline is obtained from shale as a primary product. The gasoline and other light cuts from shale oil are in many respects similar to gasoline obtained by cracking petroleum. They are highly unsaturated; the boiling point is low for a given gravity compared with that of paraffin hydrocarbons; they are a mixture of paraffins, olefines, and aromatics.[7,25] This would indicate that shale oil must compete with cracked products as to supplying gasoline. If these heavy residua can be cracked to produce motor fuels, other heavy residua can also be utilized for the same purpose. Development will be along the lines of improvement of cracking processes adaptable to such oils.

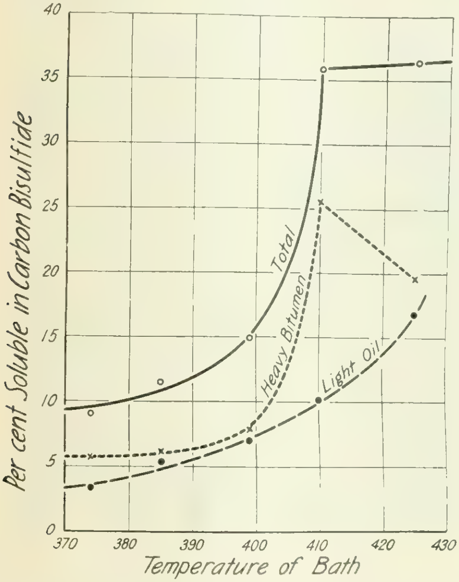


FIG. 3

Another phase of the situation is that, although gasoline is the product most in demand and the tendency is to convert other fractions into it, all of the crude cannot be used in this way, because other fractions, such as kerosene, gas oil, lubricating oil, fuel oil, and wax, are also needed. Consequently, it is the shortage in crude, and not that of gasoline, which threatens. As high-grade oils (those containing large percentages of gasoline) decrease, more gasoline will have to be produced by the cracking of heavy fractions of low-grade oils. As cracking processes improve and heavy oils are more in demand, shale oil will compete favorably as a product which can be worked up into motor fuel.

This conception has an important bearing on the commercial distillation of oil shale. It shows that there is a certain minimum temperature (which will probably vary with each shale) below which it is useless to heat and expect to recover oil at any reasonable rate. Also, when the temperature is held within the decomposition range, no gasoline is produced as a primary product. It is fallacy to say that a certain retort will yield a given amount of gasoline as a primary product. The retort should be looked upon as an apparatus for the production of heavy residua, while its efficiency as a gasoline producer should be based on its adaptability to convert these heavy oils to motor fuel. It is not meant to convey the idea that this bitumen or primary product should be removed by solvents before cracking; in fact, it is more than probable that the most effective way to crack it is while it is yet mixed with the shale residue, but the whole problem of the production of light oils should be approached from the point of view of the cracking of heavy oils.

With this information as a guiding principle, a conclusion may be reached as to the relation that shale oils will bear in making up the shortage due to the increased consumption of petroleum.

It has been shown that the light oil is obtained by the cracking of heavy products which are formed when the shale is heated to a quite definite temperature. This means that the shale retort of to-day which produces light oils is being used as a cracking still. A little consideration will show that it may be made a very efficient one.[28]

Here is a hydrocarbon formed from the decomposition of microscopic particles of material disseminated throughout a mineral mass, and this hydrocarbon is formed near the temperature at which it is subsequently cracked to form light oils. This insures uniform distribution of heat not usually met with in ordinary processes. Further, one of the most difficult problems attending the cracking of oil is the removal of the carbon formed and deposited in the still. In the Rittman process it is continually scraped down by the revolving of chains. In the Burton still it is caught on the false bottoms of the still and thus prevented from caking on the heated zone. In the case of a shale retort such, for instance, as those used in Scotland, it is being continually removed by means of a mass of mineral matter so great that the amount of carbon is insignificant.

Without the use of steam in these retorts a high oil-yielding shale will yield about 12 per cent of carbon, which will remain in a perfectly dry, finely divided condition disseminated throughout an equally dry mineral mass. This moves through the retort without difficulty, and no carbon troubles are encountered.

It is not necessary to limit the amount of bitumen passing through the retort to that which is contained in the shale. Other heavy residua, such as bottoms from previous runs or from petroleum oil, could be injected into the retort and cracked to light oil along with the shale residua. The carbon residue would be materially increased, which is desirable because it could then be used in the production of water gas or as a fuel direct. Shale residues from the straight distillation of shales are, at present, used in a gas producer for the production of fuel for retorting.[21] They are also being used as solid fuels. It need not be emphasized that additional carbon would make them more valuable.

CONCLUSIONS

It has been shown that the pyrobitumens do not decompose to form petroleum oils as a primary product of decomposition, but that the first substance obtained is a heavy solid or semisolid bitumen. This bitumen is formed at a quite definite temperature, the formation taking place between 400° and 410° C., in the case of this particular shale. The petroleum oils formed from the shale are the result of the decomposition or cracking of the heavy bitumen.

BIBLIOGRAPHY

1—Thomas Clarkson, "Facts about the Shale Oil Industry," *Oil and Gas J.*, **17** (1919), 60, No. 52.

2—M. J. Gavin, H. H. Hill and W. E. Perdew, "Notes on the Oil Shale Industry," Bureau of Mines, *Bulletin*, **1919.**

3—Greene, "Oil Shales."

4—E. H. C. Cunningham-Craig, "Kerogen Shales," *Chem. Trade J.*, **58** (1916), 360.

5—Herbert Abraham, "Asphalts and Allied Substances," **1918,** 158.

6—C. Engler, "Das Erdöl," **1** (1917), 35.

7—H. R. J. Conacher, "The Scottish Oil Shales," *Petroleum Rev.*, December **1916,** 509.

8—H. R. J. Conacher, "Oil Shales and Torbanites," *Geol. Soc. Glasgow*, Dec. 14, **1916**, 164; *Geol. Mag.*, **4** (1917), 93.

9—D. T. Jones and R. V. Wheeler, "Composition of Coal," *J. Chem. Soc.*, **109** (1916), 767.

10—D. R. Stuart, "Chemistry of the Oil Shales," "Oil Shales of the Lothians," Part 3. *Scotland Geol. Sur. Mems.*, **1912**, 136.

11—C. Engler, "Formation of the Chief Constituents of Petroleum," *Petroleum*, **7** (1912), 399; *C. A.*, **6** (1912), 1221.

12—H. M. Cadell and Grant Wilson, "Geology of the Oil Shale Fields. The Oil Shales of the Lothians," Part 1. *Scotland Geol. Sur. Mems.*, **1912**, 1–97.

13—Hardy W. Mansfield, "Oil Shales and Their Occurrence," *Petroleum Rev.*, **34** (1916), 159, 199.

14—Hardy W. Mansfield, "Oil Shales," *J. Inst. Petroleum Tech.* (London), **2** (1916), 162.

15—"Transvaal Oil-Shale Deposits," *Min. World*, **34** (1911), 74–75; *Petroleum Rev.*, **24** (1911), 147–148; *C. A.*, **5** (1911), 783.

16—J. W. McGrath, "Oil Shales of Newfoundland," *Petroleum Rev.*, **33** (1915), 209; *Can. Min. J.*, **36** (1915), 493.

17—"Bituminous Oil Shales in Canada," *Min. World*, **37** (1912), 202.

18—R. W. Ells, Can. Dept. Mines Joint Report on the Bituminous Oil Shales of New Brunswick and Nova Scotia; also on the Oil Shale Industry of Scotland, **1909**.

19—Dean E. Winchester, "Oil Shale in Northwestern Colorado and Adjacent Areas," U. S. Geological Survey (Contributions to Economic Geology), *Bulletin*, **641**-F (1916), 139.

20—G. E. Mitchell, "Billions of Barrels of Oil Locked up in Rocks," *Geog. Mag.*, **33** (1918), 194.

21—V. C. Alderson, "The Oil Shale Industry," **1920**, 31.

22—G. H. Ashley, "Oil Resources of the Black Shales of the Eastern United States," U. S. Geological Survey, *Bulletin* **641** (1917), 311.

23—Dean E. Winchester, "Oil Shales," *J. Frank. Inst.*, **87** (1919), 689.

24—C. Bardwell, B. A. Berryman, T. B. Brighton, K. D. Kuhre, "Chemical Properties of Utah Hydrocarbons," *Trans. of Utah Acad. of Sci.*, **1** (1913), 78.

25—A. H. Allen, "On the Relative Proportions of Olefines in Shale and Petroleum Products," *Analyst*, **6** (1881), 177–180.

26—C. Engler, "Formation of the Chief Constituents of Petroleum," *Petroleum*, **7** (1912), 399–403; *C. A.*, **6** (1912), 1221.

27—Herbert Abraham, "Asphalts and Allied Substances," **1918**, 57.

28—R. H. McKee and E. E. Lyder, U. S. Pat., Application No. 381,440.

Studies on the Toxicity of Wood Preservatives—III[1, 2]

By C. J. Humphrey, Ruth M. Fleming and E. Bateman

LABORATORY OF FOREST PATHOLOGY, BUREAU OF PLANT INDUSTRY, IN COÖPERATION WITH THE FOREST PRODUCTS LABORATORY, MADISON, WIS.

Since the date of our last publication[3] on this subject, petri-dish tests have been conducted on a number of wood preservatives. These preservatives have, in many instances, been prepared by the Section of Derived Products of the Forest Products Laboratory with the idea of throwing further light on the relation existing between their toxicity and chemical and physical properties.

METHOD

The petri-dish method used was essentially that described in former articles[4] on this subject.

The petri-dish cultures were placed in an incubator kept at approximately 25° C., and records of the rate and nature of growth were made every week for 6 wks. For each set of concentrations a check culture, consisting of 17 cc. of agar medium plus 3 cc. of distilled water, was prepared. The killing point was always verified once, and sometimes twice.

The fungus used was *Fomes annosus* Fr. This organism is a rapid wood destroyer and grows well on the medium used.

The petri-dish method has been followed in all the toxicity tests conducted at the Laboratory.[5] Other methods of test have been considered from time to time, such as the impregnation of wood or sawdust with varying dilutions of the preservatives, but these appear to offer no advantages over the petri-dish method, using an agar substrate, except possibly in the case of such substances as copper sulfate and zinc chloride, which may react with the agar medium.

The petri-dish method has the following advantages over other laboratory methods considered:

1—It is simple and rapid.

2—It requires little space for carrying on a large number of simultaneous tests.

3—It permits of successive growth measurements of the fungus to determine the *retarding* effect of the preservative on the organism, which data are essential in deriving mathematical equations to express the relation between toxicity and fungus growth.

4—It gives a more uniform mixture of preservative and substrate in many cases.

5—No organic solvent (diluting agent), such as alcohol, ether, etc., is necessary in order to secure the desired concentration.

In interpreting all laboratory tests on toxicity it should be kept in mind that they show only the *relative* antiseptic values of the preservatives and give an *indication* of the minimum amount necessary to prevent fungus growth.

The commercial value of a preservative depends upon a number of factors, the two more important from the standpoint of decay prevention being (1) toxicity, and (2) permanence in the wood under service conditions. Under approved impregnation methods used commercially, in order to obtain the necessary penetration the antiseptic requirements are several times fulfilled by a good preservative, such as coal-tar creosote, so that minor differences in toxicity would be overshadowed by the larger quantity of preservative introduced.

RESULTS OF THE TESTS

Table 1 gives a comparison of the toxicity of beechwood creosote, both crude and distilled, and also a comparison between the phenolic and neutral portions of fractions of the same oil.

TABLE 1—TOXICITY OF CRUDE AND DISTILLED BEECHWOOD CREOSOTE AND ITS NEUTRAL AND ACID PORTIONS

DESCRIPTION	Distillation Limits ° C.	Killing Point between (Per cent)	SOURCE
Commercial beechwood creosote, Sample 3359	....	0.12 and 0.24	
Total distillate[1] of above, Sample 3459	150°–260°	0.05 and 0.1	Distilled in laboratory
Portion of total distillate soluble in KOH, consisting of phenolic bodies, Sample 3460	180°–260°	0.025 and 0.05	Prepared in laboratory
Neutral portion of 195°–200° fraction, insoluble in KOH	195°–200°	0.2 and 0.5	Prepared in laboratory
Phenolic portion of 195°–200° fraction, soluble in KOH	195°–200°	0.075 and 0.1	Prepared in laboratory

[1] The chemical work involved in the preparation of the different fractious was done by the Section of Derived Products of the Forest Products Laboratory under the direction of Dr. S. F. Acree. In this connection see article

---

[1] Received March 14, 1921.

[2] Published by permission of the Secretary of Agriculture.

[3] R. M. Fleming and C. J. Humphrey, THIS JOURNAL, **7** (1915), 652.

[4] C. J. Humphrey and R. M. Fleming, *Ibid.*, **6** (1914), 128; see also U. S. Department of Agriculture, *Bulletin* **227** (1915).

[5] The method has been improved from time to time since the tests here recorded were made, from 3 to 5 yrs. ago. A shaking machine for mixing the agar and preservatives has been developed which is of particular advantage with the more difficultly miscible oils. Also, in the case of many of the oils, it has been found that cooling the agar-preservative mixture on ice fixes the finely divided oil particles uniformly in the medium, constituting a decided improvement. Beef extract has been entirely eliminated, since it is of no particular value for the growth of the fungi and in some cases is a detriment, and since it is objectionable on account of the combination of the proteins with certain of the preservatives.

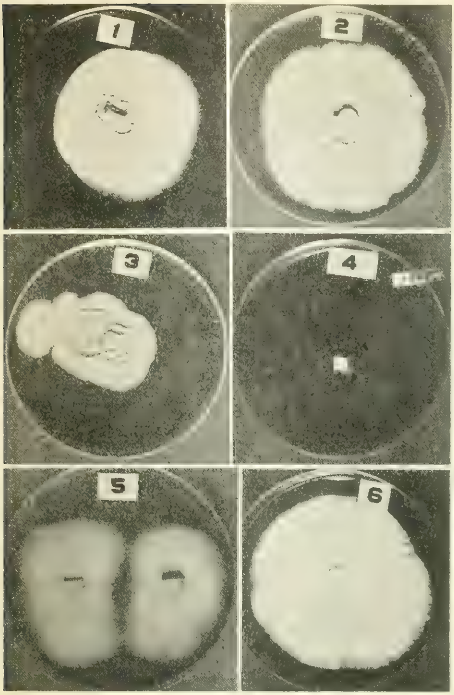


PLATE I

Fig. 1—*Fomes annosus* on 0.025 per cent concentration of KOH-soluble portion of beechwood creosote distillate, Sample 3460; after 6 wks.

Fig. 2—*Fomes annosus* on 0.05 per cent concentration of KOH-soluble (phenolic) portion of 195°–200° C. fraction of total distillate of beechwood creosote; 6 wks.

Fig. 3—Same on 0.075 per cent concentration; 6 wks.

Fig. 4—Same on 0.1 per cent; 6 wks.

Fig. 5—*Fomes annosus* on 1 per cent concentration of Cresoil, Sample B, No. 3397; 6 wks.

Fig. 6—Same on 0.05 per cent concentration of Cresoil, Sample D, No. 3399; 6 wks.

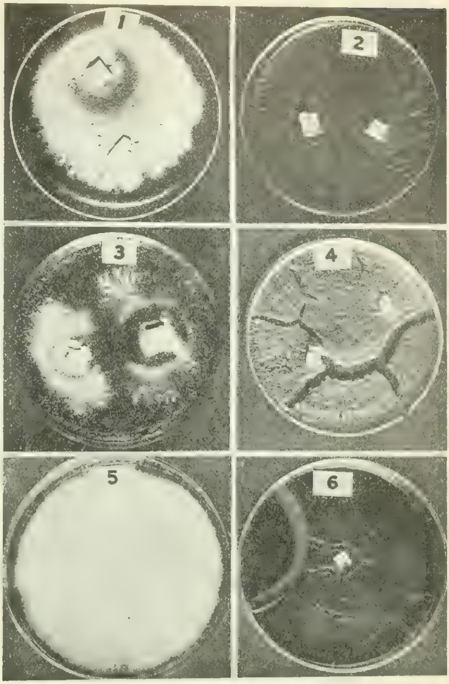


PLATE II

Fig. 1—*Fomes annosus* on 0.25 per cent concentration of 180°–185° C. fraction of beechwood creosote; after 6 wks.

Fig. 2—Same on 0.3 per cent; 6 wks.

Fig. 3—*Fomes annosus* on 0.2 per cent concentration of 185°–190° C. fraction of beechwood creosote; 6 wks.

Fig. 4—Same on 0.25 per cent; 6 wks.

Fig. 5—*Fomes annosus* on 0.1 per cent concentration of 200°–205° C. fraction of beechwood creosote; 6 wks.

Fig. 6—Same on 0.15 per cent; 6 wks.

The total distillate is fully twice as toxic as the commercial oil, and the phenolic portion of the total distillate (Plate I, Fig. 1) is again twice as toxic as the total distillate.

Comparing the phenolic portion (soluble in KOH) of the fraction whose boiling points were between 195° and 200° C., the phenolic portion (Plate I, Figs. 2–4) is again much more toxic than the neutral.

In addition to the above, fifteen fractions of the commercial beechwood creosote were prepared for toxicity tests. These fractions were taken every 5° C. from 180° to 255° C. The results of these tests are given in Table 2. The killing points were generally checked in duplicate, but this was not always considered necessary, as each killing point was more or less of a check on the one of the next higher or lower fraction.

The tests show that as the boiling point of the fractions increases there is a marked increase in toxicity up to 225° C. Above this point the toxicity of the fractions remained constant. This five-fold increase in toxicity between the 180° and the 225° fractions is probably attributable to the presence of higher boiling phenolic bodies (Plate II, Figs. 1–6, Plate III, Figs. 1–3).

TABLE 2—TOXICITY OF FRACTIONS OF BEECHWOOD CREOSOTE, SAMPLE 3359

Boiling Point of Fractions, ° C.	Killing Point between Per cent
180–185	0.25–0.30
185–190	0.20–0.25
190–200	0.15–0.20
200–215	0.10–0.15
215–225	0.075–0.10
225–255	0.05–0.075

In Table 3 is given a comparison of the toxicity of four samples of "Cresoil."[1] The toxicity of these preservatives is due to cresylic acid, and varies with the increasing amounts of this acid in conformity to Bateman's curve.[2]

This curve for coal-tar creosotes has been redrawn, changing the slope and scale somewhat, and the essential part is here reproduced in Plate IV, with the addition of a few more preservatives, including the mixtures of asphaltic oil and

---

by H. K. Smith and S. F. Acree, "A Study of Commercial Beechwood Creosote," THIS JOURNAL, 9 (1917), 275.

The toxicity data on beechwood creosote have already been published by E. J. Pieper, S. F. Acree and C. J. Humphrey, "On the Toxicity to a Wood-Destroying Fungus of Maplewood Creosote and of Some of Its Constituents and Derivatives, together with a Comparison with Beechwood Creosote," THIS JOURNAL, 9 (1917), 566.

[1] The samples described under this name were supplied by a coöperator as experimental mixtures of asphaltic oil and cresylic acid. Commercial cresylic acid is a mixture of three isomeric cresols and probably also contains both higher and lower boiling phenolic bodies.

[2] THIS JOURNAL, 8 (1916), 1094; also *Wood Preserving*, 3 (1916), 83.

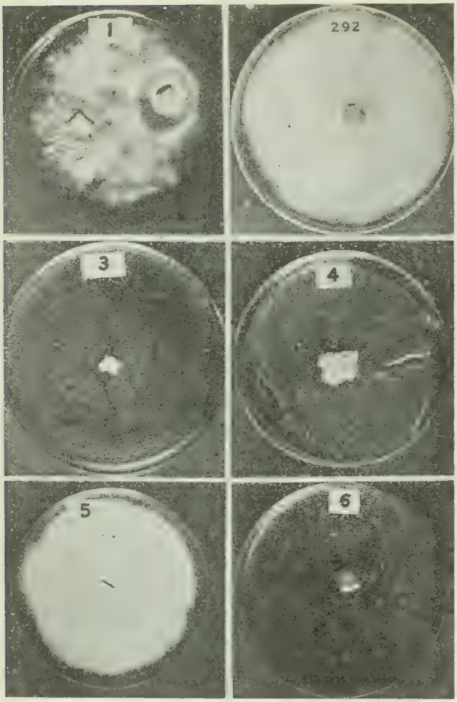


PLATE III

Fig 1—*Fomes annosus* on 0.15 per cent concentration of 190°-195° C. fraction of beechwood creosote, after 6 wks.

Fig. 2—*Fomes annosus* on 0.05 per cent concentration of 250°-255° C. fraction of beechwood creosote; 6 wks

Fig. 3—Same on 0.075 per cent; 6 wks.

Fig. 4—*Fomes annosus* on 0.2 per cent concentration of Grade I Creosote, Sample No. 3352; 6 wks.

Fig. 5—*Fomes annosus* on 0.1 per cent concentration of a commercial preservative, Sample No. 3357; 6 wks.

Fig. 6—Same on 0.2 per cent; 6 wks.

TABLE 3—TOXICITY OF FOUR MIXTURES OF ASPHALTIC OIL WITH CRESYLIC ACID

PRESERVATIVE	DESCRIPTION	Ratio of Cresylic Acid to that in Sample D	Ratio of Toxicity to that of Sample D	Killing Point Per cent
Sample A, 3396	95% Asphaltic oil 5% Cresylic acid	0.0526	0.0286	3.5
Sample B, 3397	93% Asphaltic oil 7% Cresylic acid	0.0737	0.0714	1.4
Sample C, 3398	90% Asphaltic oil 10% Cresylic acid	0.1053	0.1000	1.0
Sample D, 3399	5% Asphaltic oil 95% Cresylic acid	1.000	1.000	0.1

cresylic acid, and other mixtures of coal-tar creosote and gas oil to be described later.

It will be noted from the curve that the four Cresoil samples fall either directly on the curve or very close to it. In plotting this curve it was assumed that all the cresylic acid would distil below 275° C., in which case the curve as plotted is really a concentration-toxicity curve as well as a volatility-toxicity curve. This leads one to the rather interesting hypothesis that the toxicity curve is in reality only a curve obtained by the solubility of cresol in oil and water. If we assume that the toxicity as tested in the petri dish is due to minute quantities of cresol which are soluble in water and that the different killing points recorded for the different concentrations of Cresoil give a water solution of the same toxicity at the killing points, we can then calculate the concentration of the water solution, as well as the concentration of the oil solution when the equilibrium is reached. These calculations have been made, and the curve reproduced from these values is practically identical with the toxicity-volatility curve of coal-tar creosotes. Attempts are now being made to check up the values for the concentration of the water solution, by very careful experiments in the chemical laboratory. If this curve is correct it opens up a new line of thought on the value of oils in wood preservation.

Another interesting phase of the problem which has developed in our work is the fact that dilutions of coal-tar creosote with a practically inert oil (gas or petroleum oil) bear out the same relations of toxicity to volatility. The data on the three mixtures tested are recorded in Table 4 and are also shown on the curve.

TABLE 4—RELATION BETWEEN TOXICITY AND VOLATILITY OF COAL-TAR CREOSOTE CONTAINING DIFFERENT AMOUNTS OF GAS OIL (PETROLEUM OIL) AS A NONTOXIC DILUTING SUBSTANCE

PRESERVATIVE	COMPOSITION	Killing Point Per cent	Proportion of Coal-Tar Creosote Present	Toxicity Ratio[1] to Coal-Tar Creosote No. 1074	Volatility[2] Per cent Distilling below 275° C.	SOURCE
Coal-tar creosote No 1074	Grade C of A R E & M W Ass'n	0.35	100	100	54.1	Commercial sample
Coal-tar creosote, No 1074 (diluted)	50% Coal-tar Creosote + 50% Gas oil	Between 0.5 and 0.7	50	50	27.0	Prepared at this laboratory
Coal-tar creosote, No 1074 (diluted)	10% Coal-tar creosote + 90% Gas oil	Between 8 and 9	10	4	5.0	Prepared at this laboratory

[1] The ratio is determined from the higher limit of the killing point.

[2] The gas oil dilution is not considered in reckoning the volatility, the volatility of the dilutions being calculated from the proportion of creosote present.

These data may prove of considerable practical value as indicating that the dilution of a high-grade creosote, containing sufficient low-boiling constituents, does not necessarily impair its toxicity to a very serious extent if the dilution is not carried above 50 per cent. However, the writers do not wish to present this as more than a hypothesis, for the preserving action of creosote is not necessarily entirely dependent on its toxicity. It might very well hold

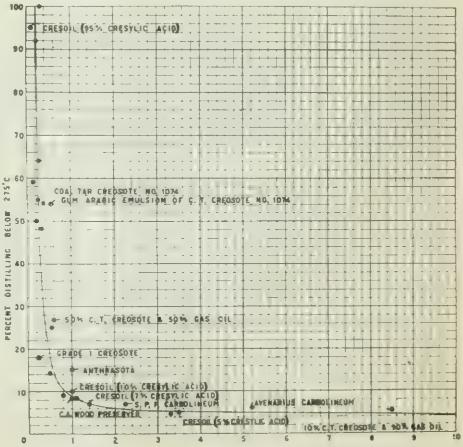


PLATE IV

that an excess of the highly toxic, low-boiling constituents would be necessary under service conditions to act as a reserve to compensate for leaching and evaporation.

Table 5 gives a list of five commercial preservatives sent to this laboratory to be tested.

Sample IV proved to be the most toxic substance we have yet tested. Probably its toxicity lies for the most part in the 23.8 per cent of dinitrophenol which it contains. Falck[1] found that it required less than 0.02 per cent of *o*-nitrophenol and less than 0.01 per cent of either *p*-nitrophenol or the sodium salt of the 2,4-dinitrophenol to kill *Coniophora cerebella*, which is a very destructive wood-destroying fungus.

TABLE 5—TOXICITY OF VARIOUS COMMERCIAL PRESERVATIVES

PRESERVATIVE	DESCRIPTION	Sp. gr. at 38° C.	Killing Point Per cent
Anthrasota, Sample 3353	A brownish-black mild liquid sold as a high-boiling coal-tar distillate; 15.1% distils below 275° C.	1.115	Between 0.9 and 1.1
Grade I Creosote, Sample 3352	Sold as a high-boiling coal-tar distillate; 18% distils below 275°	1.089	Between 0.2 and 0.3
Wood Preservative, "Conservo"	A brown oily liquid; sold as high-boiling nonvolatile coal-tar oils and other preservative salts	. . .	Between 0.1 and 0.15
Mykantin, Sample 3393	A brownish green paste soluble in water; 23.8% dinitrophenol	. . .	Below 0.01
Preservol, Sample 3357	A black pungent wood distillate containing 4.1% acid (calc. as acetic); 88.5% distils below 265° C.; water 10.8%	1.058	Between 0.1 and 0.2

The remaining oils, with the exception of Sample I, which is a carbolineum of somewhat higher boiling point than the Grade I creosote, proved highly toxic. The results on the coal-tar products are plotted on the curve in Plate IV.

The Toxicity of Various Fractions and Combinations of Fractions of Coal-Tar Creosote to Wood-Destroying Fungi[2,3]

By Henry Schmitz and Sanford M. Zeller

SCHOOL OF FORESTRY, UNIVERSITY OF IDAHO, MOSCOW, IDAHO, AND OREGON AGRICULTURAL COLLEGE, CORVALLIS, OREGON

Considerable work has been done in the past to determine the toxicity to wood-destroying fungi of various fractions of coal-tar creosote and many other wood preservatives. However, much of this work is of little or no practical importance for either of two reasons: First, wood impregnated with the creosote was not used as the substrate, and, second, the minimum percentages of single fractions are of little or no concern, but rather a combination of certain fractions with the elimination of certain others. That is, the most probable result which obtains after a creosoted timber is exposed to natural weather conditions is the evaporation and leaching of the lighter and more soluble parts of the mixture.

Among the later workers in this field are Humphrey and Fleming,[4] who determined the toxic point of some fractions of creosote, but who used single fractions in all cases and combined them with nutrient agar, conditions in no way comparable with those in actual practice. The literature regarding this line of investigation has been sufficiently reviewed in the paper just cited so that no review will be made here. The discrepancies between the so-called petri-dish method used by the above-mentioned writers and the conditions met with in treated timbers are obvious. In the first place, the emulsion which is formed when creosote and agar are thoroughly mixed is by no means permanent, and, even in *very rapid* cooling of the agar after the emulsion has been formed, it is quite probable that the individual minute droplets have coalesced to form droplets of considerable size resulting in a more or less irregular mixture varying from globules of the insoluble portions of the creosote to nutrient agar containing varying proportions of the water-soluble portions of the creosote mixture. In the second place, it is a well-known fact[5] that the toxicity of a certain substance may be altered materially by the presence of other substances. This may be particularly true where there are such complex relations as would exist between emulsions, colloids, electrolytes, and non-electrolytes, such as are found in an emulsion of coal-tar creosote in nutrient agar. On the other hand, the use of impregnated wood as a culture medium for fungi causing wood decay offers no particular difficulty, and there is more valid reason than not why wood should be used in preference to synthetic media. It has seemed to the writers that sawdust, although not physically the same as solid wood, is the most appropriate medium for the culture of wood-destroying fungi in such studies as are presented here.

METHODS

In the present study, creosote (von Schrenk and Kammerer No. 3072) derived from coal tar was used. This oil, when analyzed[1] according to the method[2] now standard in the American Railway Engineering Association, the American Wood Preservers' Association, and the American Society for Testing Materials, gave the following results:

Sample No.	3072
Sp. gr. at 38° C.	1.048
Water	0.0
DISTILLATION TEMPERATURE ° C.	Per cent
210	3.6
235	32.4
270	23.8
315	16.9
355	15.4
Residue	7.9
TAR ACIDS	
Per cent by volume	7.5
Sp. gr. fraction, 235°–315°	1.038
Sp. gr. fraction, 315°–355°	1.100

FRACTIONATION—For the experimental work here recorded, the creosote was fractionated as follows:

1—Undistilled.
2—Fraction below 210° C.
3—Fraction between 210° and 235° C.
4—Fraction between 235° and 270° C.
5—Fraction between 270° and 315° C.
6—Fraction between 315° and 355° C.
7—Residue above 355° C.
8—Combination of all fractions, except below 210° C.
9—Combination of all fractions, except between 210° and 235° C.
10—Combination of all fractions, except between 235° and 270° C.
11—Combination of all fractions, except between 270° and 315° C.
12—Combination of all fractions, except between 315° and 355° C.
13—Combination of all fractions, except residue above 355° C.

---

[1] Alfred Moller, "Die Merulius-fäule des Bauholzes." In "Hausschwammforschungen," **6** (1912), 355.

[2] Received March 21, 1921.

[3] This work was begun in the Research Laboratories of the Missouri Botanical Garden and completed in the Laboratory of Forest Products, School of Forestry, University of Idaho. Thanks are due to the Missouri Botanical Garden for the privileges of the laboratories, and to Doctor Hermann von Schrenk for suggestions.

[4] "The Toxicity to Fungi of Various Oils and Salts, Particularly Those Used in Wood Preservation," U. S. Department of Agriculture, *Bulletin* **227** (1915), 1, Plates 1–3.

[5] A Le Renard, "Influence du Milieu sur la resistance du *Penicille crustace* aux substances toxiques," *Ann. sci nat bot*, [**9**] **16** (1912), 277.

[1] Thanks are due to Dr A. L. Kammerer, Consulting Timber Engineer, St. Louis, for making this analysis and for fractionating the creosote and combining the various fractions.

[2] *Proc. Am. Wood Preservers' Assoc.*, **1917**, 309.

PREPARATION OF MEDIA—All fractions and combinations of fractions were entirely soluble in 95 per cent ethyl alcohol, except the residue above 355° C. The following method was therefore employed: Twice the maximum concentration (calculated in weight of creosote to weight of air-dried wood) of creosote was dissolved in 100 cc. of redistilled 95 per cent ethyl alcohol. One-half of this alcoholic solution was added slowly and with constant stirring to 20 g. of air-dried yellow poplar (*Liriodendron tulipifera*) sawdust in a large beaker. This amount of alcohol was just sufficient to saturate the sawdust so that no free liquid remained, and an evenly impregnated sawdust was obtained.

The remaining 50 cc. of alcoholic solution were diluted to 100 cc. with alcohol, giving a concentration of creosote equal to one-half the former. This procedure was carried on throughout the range of concentrations used. The impregnated sawdust was spread out on clean glass plates for 24 hrs., in which time all of the alcohol had evaporated. The sawdust now weighed exactly 20 g. plus the weight of the creosote calculated for each dilution. Hence, no creosote was lost during the 24-hr. exposure to the air. Even had there been a little loss in weight, this would have been of no practical importance, since substances so volatile that they would be lost in so short a time would be of little or no practical importance in timber preservation.

The same procedure was followed in the experiments where western white pine (*Pinus monticola*) sawdust was substituted for the yellow poplar sawdust.

To prepare intermediate concentrations of creosote in sawdust, equal amounts of others were mixed. For example, a 3 per cent concentration was prepared from equal amounts of the 2 and 4 per cent material. In some cases, however, it was also necessary to make a new series of dilutions.

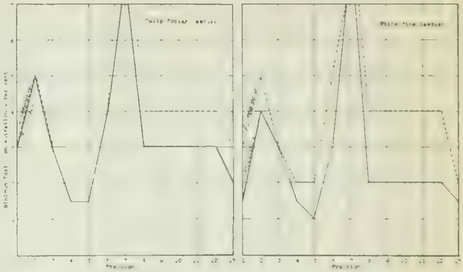
As has been said, one fraction (the residue above 355° C.) was not entirely soluble in alcohol. In this case, the same procedure was employed and the remaining insoluble substances were added proportionately by weight to the various flasks.

After the alcohol had evaporated, 3 g. of the impregnated sawdust were placed in each of four 8-oz. bottles. Twenty cc. of distilled water were then added to each bottle containing the white pine, while 12 cc. of water were added to each of the flasks containing the tulip poplar sawdust. In each case this amount of water was just sufficient to saturate the sawdust thoroughly without any free water remaining.

STERILIZATION—The media were sterilized as follows: The bottles were tightly corked with suberin stoppers surrounded by heavy paraffined paper and placed in a rigid wooden frame into which the corked bottles would fit tightly, so that there would be no possible chance of the corks blowing out or becoming loose while being autoclaved. All of the bottles were autoclaved for 20 min. at 20 lbs. pressure. Immediately after autoclaving, the corks were removed and previously sterilized cotton plugs were substituted under sterile conditions to avoid all possible chances of contamination. The bottles were then ready for inoculation.

A check was run on this method of sterilization in order to determine whether any creosote was lost during the process of autoclaving. A series of culture bottles (not including the corks), prepared as above described and carefully weighed to the fourth decimal place before and after autoclaving, showed no loss in weight.

PREPARATION OF CULTURES—The fungi used were *Polyporus lucidus* (Leys.) Fr. and *Lenzites saepiaria* Fr. Duplicates were prepared for each concentration of creosote. Three control sets were also prepared for each wood, one with natural sawdust, a second with sawdust treated with alcohol at the rate of 50 cc. per 20 g. of sawdust, and a third with sawdust treated with alcohol at the rate of 100 cc. per 20 g. of sawdust. In each case the alcohol was evaporated as previously described by spreading the sawdust on a glass plate and exposing the latter to the air for 24 hrs.



TOXICITY OF THE VARIOUS FRACTIONS AND COMBINATIONS OF FRACTIONS OF COAL-TAR CREOSOTE TO *Lenzites saepiaria* AND *Polyporus Lucidus*

The culture bottles were inoculated by means of small squares of agar from plate cultures of the respective fungi. After inoculation, the bottles were incubated at 28° C. until the sawdust in the control flasks was entirely permeated with the fungous mycelium. This required about 18 days in the case of *Polyporus lucidus* and about 25 days in the case of *Lenzites saepiaria*. Growth was also slower on the white pine sawdust than on the tulip poplar sawdust. The cultures were carefully examined with a hand lens to determine whether, and if so to what extent, the mycelium had permeated the sawdust. In the foregoing curves the minimum toxic concentration expressed in per cent dry weight of the sawdust is shown on the abscissas.

DISCUSSION OF RESULTS

The data are self-explanatory. The results indicate no toxic effects of any single distilled fraction or combination of fractions of the coal-tar creosote below a concentration of 1 per cent, calculated on the weight of air-dried sawdust. That is, there was no visible cessation of growth of either *Lenzites saepiaria* or *Polyporus lucidus* below a 1 per cent concentration. In a majority of cases, the toxic point, which we have defined as the minimum percentage of the creosote which will completely inhibit the growth of the organisms, lies between 2 and 4 per cent. Because of the discrepancies between the two methods, as pointed out elsewhere in this paper, the results of our experiments are at variance with those obtained by Humphrey and Fleming.[1] This was to be expected, and a comparison of the results could not be beneficial here because of the many factors which would naturally lead to differences in results. The comparison of the results of the two methods can only be left to their merits in practical application, and either one may be discarded if a preferable method is suggested for the testing of the toxicity of wood preservatives.

From the data obtained, it is evident that *Lenzites saepiaria* is more resistant to greater concentrations of coal-tar creosote than is *Polyporus lucidus*. As would be expected, the percentage of creosote necessary to inhibit the growth of wood-destroying fungi varies with the wood. The two most toxic fractions are those which distil over between 235° and 270° C. and between 270° and 315° C. There is no great difference in the toxicity of any of the combinations of the various fractions except when the residue above 355° C. is omitted. Since this residue is toxic only in very high concentrations, its absence from the combination of the others would tend to increase their united toxicity.

---

[1] *Loc. cit.*

It may be argued that the computed percentages of creosote, calculated on the basis of dry weight of the sawdust, are not the actual values which should be taken into consideration because of the amount of water present during the growth of the organisms. However, we feel that there would be little in favor of such an argument when compared with actual practice. In commercial practice the amount of impregnation is calculated as pounds of creosote per cubic foot of wood, seasoned either before or during the process of impregnation. Thus, the percentage of creosote ultimately becomes a question of weight, depending upon the specific gravity of the wood. Moreover, in actual practice, impregnated timbers, such as railroad ties, may be placed under moisture conditions very favorable to the support of fungous growth. Under these conditions, moisture would be absorbed by the wood. The present experiments were attempts to imitate these natural conditions which are conducive to timber decay.

Nitrocellulose and Its Solutions as Applied to the Manufacture of Artificial Leather[1]

By W. K. Tucker

Hercules Powder Co., 12 Forbes St., Worcester, Massachusetts

Although nitrocellulose has been used in the manufacture of artificial leather for a good many years, very little has been printed which is of practical value to anyone wishing to make a study of the business. This has been due partly to the desire of those who have had practical experience to profit personally by their knowledge, and partly because many who have had the requisite experience have not been scientific men and have worked roughly by rule of thumb, being entirely unfamiliar with the underlying principles. The facts presented in this paper have long been known to scientific and practical men in the artificial leather business, but so far as I know have not been published, and are of interest to industrial chemists.

Viscosity of Solutions

The first important point to be considered in the use of nitrocellulose for this purpose is viscosity. In discussing the viscosity of nitrocotton it is always understood that reference is made to the viscosity of a 16-oz. solution of nitrocotton in some solvent. This standard solution is made by dissolving 16 oz. of nitrocellulose in a gallon of solvent. A certain increase in volume occurs during this process so that the standard 16-oz. solution contains somewhat less than 16 oz. of nitrocotton to the gallon of solution. For instance, in one of our standard solutions 16 oz. of nitrocotton added to 1 gal. of the mixture of solvents and non-solvents produced 1.965 gal. of solution, containing 12.2 per cent of nitrocotton. If the solution actually contained 16 oz. of nitrocellulose to the gallon the percentage would be 13 per cent.

The viscosity of nitrocellulose is determined by noting the time taken for a steel ball five-sixteenths in. in diameter to drop through a 10-in. column of a 16-oz. solution of the material in question. This would appear to be a simple method and one that could be used by any manufacturer. Unfortunately, a great deal of confusion occurs when customers order cotton specifying the viscosity by this method, because there is no standard solvent generally used for such a test, and varying temperatures and the size of the container affect the result. In this laboratory we use a standard 16-oz. solution (*i. e.*, 16 oz. of cotton to the gallon of solvent), and the solvents are roughly 70 per cent ethyl acetate and 30 per cent benzene. A standard container, large enough in diameter to prevent any effects of friction from the displacement of the solution, is used, and the test is made at 25° C.

In general, this is the method used by large consumers and manufacturers of nitrocellulose to determine viscosity, and it is accurate enough, providing the mixture of solvents and the apparatus be standardized so that conditions are identical when the test is made by the manufacturer and consumer. If this Society could get together the data required and standardize the method, a great service would be rendered to the industry, eliminating many unfortunate mistakes and misunderstandings.

It may be noted here that most of the cotton used for the manufacturing of artificial leather is of low viscosity. The problem is to fix the required amount of cotton and other solids on a cloth base with the least loss of solvents. As the viscosity of the final solution as applied is fixed within rather narrow limits by the coating machine, and as the solution must be as inexpensive as possible, it is obvious that a cotton is desirable which will allow of the addition of a large amount of cheap non-solvent, such as benzene, and yet not bring the viscosity of the solution above the set limits (*i. e.*, about 40 sec.). As the addition of non-solvents always increases the viscosity of a solution, the low viscosity cotton is logically the grade most suitable, since it will admit of the addition of the most non-solvent.

Although the manufacture of nitrocellulose of various viscosities is too big a subject to enter into in this paper, the following generalities can be mentioned. A high viscosity cotton usually results from a high nitrogen content, or from a low temperature during nitration, while a high nitrating temperature or a long nitration results in a low viscosity product.

The industry uses nitrocotton of three viscosities: low, from 5 to 20 sec.; medium, from 40 to 60 sec.; and high, from 100 to 2400 sec. The greatest demand is for a material of about 20 sec. The higher viscosities are generally used for blending purposes to bring the viscosity of a certain solution up to the required point.

Degree of Nitration

Roughly stated, the problem is to place a certain amount of nitrocotton on the surface of the cloth with the least waste of solvents.

The second point to be considered is the conditions of nitration desirable in nitrocellulose to be used in the making of artificial leather. This is determined by the fact that varying degrees of nitration affect its solubility in the commonly used solvents.

The nitrogen content of such a material averages about 12 per cent, although a range of from about 11.5 to 13 per cent is allowable. Roughly speaking, the lower the nitrogen content between these limits, the greater the solubility, and consequently the greater the amount of non-solvents which can be used in solutions. If the nitrogen content goes above or below these limits, the solubility of the nitrocellulose in the usual solvents decreases; less non-solvents can be used, and finally particles of cotton fail to go into solution, remaining suspended in the solution.

Stabilization

The third point to consider is the question of stabilization and bleaching which are required after nitration. Except where cotton is to be used for making a white artificial leather, the question of color is not of the highest importance. Nevertheless, it is desirable to give the material a very thorough treatment in the boiling tubs, and produce a cotton which can be used on any grade of artificial leather. Opinion varies as to the importance of stability in nitrocellulose to be used for this purpose, but it is generally acknowledged that an unstable product will cause cracking of the film in the finished leatherette.

---

[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

It is to be noted that the stabilization and pulping processes have a decided lowering effect on the viscosity of nitrocellulose, so that in making a cotton to meet a specified viscosity this element must be taken into account. Also this effect can be utilized to reduce the viscosity where it is found to be too high.

The test for ash is of minor importance where the nitrocellulose is to be used for the manufacture of artificial leather. Nevertheless, it is always made, as an excessive ash indicates the presence of too much dirt. A good grade of soluble cotton should not have over 0.4 per cent ash.

SOLVENTS

In making up solutions for the manufacture of artificial leather, two solvents are very generally used: acetone oils and ethyl acetate. The commercial acetone oils consist largely of methylethylketone, with some acetone and higher ketones, as well as small quantities of condensation products, such as mesityl oxide. The non-solvents are usually benzene or benzine. As nitrocellulose is usually shipped wet with denatured alcohol, this latter material is nearly always present in the final solution. Although not a perfect solvent for nitrocotton, alcohol tends to lower the viscosity of a solution. A typical artificial leather solution rarely contains more than 30 per cent acetone oils or other solvent, the remainder consisting of benzene, etc. This percentage is often reduced even to 10 per cent.

It used to be considered necessary to have present a certain amount of high boiling solvent, such as amyl acetate, ethyl propionate, etc., but most manufacturers now get along without its presence, and some claim that such a solvent actually tends to produce pinholes in the finished leather. This, they think, is caused by the higher boiling solvent remaining in the coat until most of the other solvents and non-solvents have evaporated. The non-use of high boiling solvent is, of course, made possible only by the use of a mixture in which the boiling point of the solvent is higher than that of the non-solvent, or where their boiling points are very nearly the same, as otherwise the rate of evaporation of the solvent during the drying process would be greater than that of the non-solvent. In such a case a point would be reached where the percentage of non-solvent would be high enough to precipitate part of the nitrocotton and cause blushing of the film and a consequent flaking off of the coat.

The solutions usually used by manufacturers have a viscosity of about 40 sec. It is interesting to note that the solvents and non-solvents used have a decided effect on the viscosity of a solution. In general, it may be stated that solvents of higher molecular weight make a more viscous solution when nitrocotton is dissolved in them than do those of lower molecular weight. Thus, solutions in ethyl propionate, ethyl butyrate, butyl acetate, or amyl acetate are of higher viscosity than solutions of the same nitrocellulose in acetone or ethyl acetate. The introduction of any non-solvent always increases the viscosity of the resultant solution. Thus, nitrocellulose which will give the standard 16-oz. solution a viscosity of 20 sec. when dissolved in a mixture of 70 per cent ethyl acetate and 30 per cent benzene will give a viscosity of about 40 sec. when the percentage of benzene is 70 and that of the ethyl acetate 30.

Solutions in which the viscosity is too high are generally known as "short" solutions. "Granular" solutions are those which are hazy and in which all the nitrocellulose has not dissolved. These latter are usually caused by either over- or under-nitration of the cotton, making it partly insoluble in the usual solvents.

There exists a good deal of difference of opinion as to the relative advisability of using a 16-oz. solution or one where the nitrocotton content is higher, such as a 20- or 24-oz. solution. The majority of manufacturers seem to use the 16-oz. solution, but there are notable exceptions. Men well up in the business declare that the cost of manufacture depends largely on cost of materials, the labor element being small. It would appear on the surface, then, that if an artificial leather of the same weight could be made by the application of fewer coats of a dope containing more nitrocotton, considerable economy might be effected in the saving of solvents. However, there are a good many factors to consider. A 24-oz. solution would have to be considerably richer in solvents to give a viscosity of 40 sec. than a 16-oz. solution giving the same viscosity. That is, the proportion of cheap non-solvent would have to be decreased, and the mixture would rise in cost per gallon. Reducing the viscosity of the cotton used would not be very advantageous, as the extremely low viscosity cotton is uneconomical to manufacture on account of the low yields and danger of fires. Some also claim that the heavier solutions tend to produce more pinholes in the finished goods. Probably there is room for difference of opinion on this point, and a practical man who has developed a good product using a certain weight solution is naturally averse to making a change. After the nitrocellulose and the solutions are brought up to a satisfactory standard, a great deal has yet to be done to turn out a high-grade artificial leather, and it is here that the actual practical operator has a field for valuable experimental work.

Monthly Statistical Service on Production and Stocks of Sulfuric Acid and Nitric Acid

The Department of Commerce, through the Bureau of the Census, is preparing to issue monthly reports on the production and stocks of sulfuric acid and nitric acid. Secretary Hoover has been assured of the coöperation of the manufacturers of these products, and Mr. Steuart, Director of the Census, is consulting them as to the form of schedule that will yield the required data with least inconvenience to the industry. The data secured from firms and corporations will be held as confidential, totals only being published.

The purpose of the Department in issuing monthly reports of this character is to assist in the stabilization of industry by furnishing such aid as may be possible by the dissemination of information necessary to intelligent procedure. The undertaking is endorsed by the Manufacturing Chemists' Association, and by many officials of corporations engaged in the production of these acids. This is an opportunity for the chemical industry to secure an important service from the Department of Commerce, and it is recommended that all manufacturers who receive the schedule give it prompt attention and assist in the compilation of reports that can be distributed shortly after the end of the month to which the figures relate.

Insecticide and Disinfectant Manufacturers Association

The recent meeting of the Insecticide and Disinfectant Manufacturers Association at Atlantic City, June 13 and 14, 1921, was a success from the point of view of attendance and interest shown. Among the guests who addressed the Association was Mr. W. D. Hartley, representative of McDougall Bros., Ltd., Manchester, England, who discussed informally trade conditions in England.

An Experimental Study of the Significance of "Lignin" Color Reactions[1,2]

By Ernest C. Crocker

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

There are certain color reactions[3] given by wood and lignified fibers, and not by thoroughly cooked pulp, which are commonly considered by paper-mill chemists and others who work with these substances as more or less specific tests for lignin.

In connection with an investigation carried out in this laboratory for the Mead Research Co., of Dayton, Ohio, with regard to some coloring matters in wood, it was felt desirable to have information concerning the substance or substances in wood responsible for these color reactions. The literature[4] upon this subject, while quite voluminous, was found to be contradictory and incomplete in many places, so that it became necessary to make an experimental study of the problem. While this involved some duplication of previous work, it is believed that the results may be of interest, since purer reagents were used than were available to some of the early investigators, and the method of attack of some phases of the problem was different. The Mead Company has kindly given its permission for the publication of the results obtained. The experimental work, here briefly summarized, was carried only far enough to arrive at an answer to certain practical questions. The field, however, is broad enough for more work, some of which should be of interest to the paper and allied industries.

The color reactions investigated most thoroughly were those of wood with phloroglucinol, aniline, *p*-nitroaniline, and pyrrole, the Mäule reaction, and the ferricferricyanide reaction.[5] These tests were varied in such ways as to aid in determining the essential components both of wood and reagent responsible for the tests.

The Action of Phloroglucinol and Other Phenols on Wood

Phloroglucinol solutions were made up in the customary way, by dissolving 1 to 2 per cent of the material in 6 *N* aqueous hydrochloric acid, and in 6 *N* hydrochloric acid in 50 per cent alcohol.

Some of the above reagents were applied to several kinds of deciduous and coniferous woods, and to the woody fiber of the achlorophyllous plant, *Monotropa uniflora* (Indian pipe). In each case, a strong red color was produced in a few moments.

The reagent containing alcohol did not give such strong or clean-cut tests as the one containing only water, as the alcohol caused spreading of the stain.

Other solutions were made up with sulfuric acid of various strengths. It was noted that the stronger the acid the quicker the reaction. From 20 per cent to 70 per cent sulfuric acid were found to be effective as a reagent, but in no way better than strong hydrochloric acid.

As many phenols other than phloroglucinol are mentioned in the literature as being effective as reagents, a considerable number were tried out, in 6 *N* hydrochloric acid, in 10 *N* hydrochloric acid, and in 50 per cent sulfuric acid.

Making the tests on various kinds of wood, strong red, violet, or blue colors were obtained in the cases of orcinol, resorcinol, and pyrogallol. Pale greenish or brownish colors only, or no coloration, were obtained with phenol, guaiacol, thymol, eucalyptol, α- and β-naphthols, *p*-nitrophenol, *m*-nitrophenol, picric acid, hydroquinol, pyrocatechol, gallic acid, and tannic acid.

Certain phenols which had two hydroxyls meta to each other produced strong red to blue colors. These were, in the decreasing order of rapidity of color formation: phloroglucinol $\longrightarrow$ orcinol $\longrightarrow$ resorcinol $\longrightarrow$ pyrogallol.

The Action of Various Amines on Wood

Aniline and *p*-nitroaniline solutions in dilute hydrochloric acid were found to give yellow and orange stains, respectively. The acid strength was increased and decreased, and the rapidity of staining noted. In every case where there was excess free acid, the stain was readily produced. Other amines were then tried, all in 2 *N* hydrochloric acid, with the results listed below:

Yellow or orange-yellow colors were given by aniline, monomethylaniline [faint], α-naphthylamine, *m*-aminophenol, anthranilic acid, sulfanilic acid, *o*- and *p*-toluidines, phenylhydrazine, and dimethyl-*p*-phenylenediamine. Orange colors were given by *p*-nitroaniline and diphenylamine, and a deep red color by pyrrole. No color was given by formamide, acetamide, urea, acetanilide, dimethylaniline, carbazole, or pyridine. (The diphenylamine was purified by recrystallization from 70 per cent alcohol, and by treatment, in the molten state, with dilute hydrochloric acid, to remove any traces of primary amines.)

These experiments indicate that most, if not all, aromatic primary amines, and at least diphenylamine among the secondary amines, react with a component of wood to form colored compounds. Acid amides do not react, and no reactive tertiary amine has been found. Only a small concentration of free acid is needed for the reaction.

Study of Compounds Which Give Colors with Phenols and Amines

Phloroglucinol in 6 *N* hydrochloric acid and aniline in 2 *N* (free) acid were used as reagents to add to small amounts of chemicals on a porcelain spot plate, and to alcoholic solutions containing one-tenth of their volume of concentrated hydrochloric acid. (It was noted that in any case where a color was formed on the spot plate, it was also formed in alcoholic solutions and vice versa.)

The colors given with these reagents are shown in the accompanying table.

Substance	Color with Phloroglucinol	Color with Aniline
Wood	Strong cerise	Strong yellow
Eugenol (oil of cloves)	Strong cerise	Strong yellow
Eugenol methyl ether	Strong cerise	Strong yellow
Safrol (oil of sassafras)	Strong cerise	Strong yellow
Salicyl aldehyde	Strong scarlet	Strong yellow
Vanillin	Scarlet	Yellow
Piperonal	Pink	Faint yellow
Cinnamic aldehyde	Strong orange	Yellow
Cinnamic alcohol	Strong orange	Yellow
Anisaldehyde	Orange	Faint yellow
Furfural	Orange $\rightarrow$ olive $\rightarrow$ black	Strong yellow
Citral	Orange	Faint yellow
Citronellal	Orange $\rightarrow$ pink $\rightarrow$ colorless	Faint yellow
Benzaldehyde	Buff	None
Anethole	Pale orange	None
Heptaldehyde	Pale orange	None

No color appeared with either phloroglucinol or aniline in cases of formaldehyde, acetaldehyde, duodecylaldehyde, anisole, phenol, resorcinol, hydroquinol, pyrogallol, pyro-

---

[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Contribution No. 32 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] A. Klein, *Papier-Ztg.*, **34** (1909), 267; *Paper*, **24** (1919), 351.

[4] V. Grafe, *Monatsh.*, **25** (1904), 987; F. Czapek, "Biochemie der Pflanzen," Jena, **1913**.

[5] R. Haller, *C. A.*, **10** (1916), 530

catechol, thymol, eucalyptol, glucose, cinnamic acid, and benzoic acid.

Among the compounds conceivably present in wood which gave no colors with either phloroglucinol or aniline were many simple phenols, polyphenols, alcohols, acids, and the modified aldehyde, glucose.

All the substances which gave the color tests strongly were pure aldehydes, except for a few materials derived from vegetable sources, where there was opportunity for contamination with any materials present in the plant from which they were obtained. In order to determine whether the colors given by these compounds might be due to traces of aldehydic impurities, the eugenol, safrol, eugenol methyl ether, and cinnamic alcohol were each shaken up with saturated sodium bisulfite solution for some time and then separated. This treatment was repeated five or six times, and the essentially aldehyde-free materials were again tested. In each case, the color-forming power was very greatly reduced, and in the case of eugenol methyl ether, practically eliminated. The aldehyde-reduced eugenol was tested when freshly treated, and again after four months had elapsed. In each case, the amount of color produced was about 5 per cent of that given by the untreated eugenol, indicating that air-oxidation was not responsible for the aldehyde in eugenol which gave the color with "lignin" reagents.

Eugenol was treated with phloroglucinol plus hydrochloric acid, and steam-distilled from this mixture. It gave no coloration whatever with phloroglucinol and no yellow with aniline. After steam-distillation from aniline and hydrochloric acid, eugenol gave a faint orange color with phloroglucinol, which, on standing, became greenish. (This is an evidence of a trace of furfural in the eugenol, which was not held by the aniline.)

Many of the references in the literature to color reactions with phloroglucinol, on the one hand, and eugenol, safrol, cinnamyl alcohol, anethole, and anisole, on the other, were doubtless due to the presence of aldehydic impurities in the reagents used. (Anethole and anisole, as tested in this laboratory, gave no color whatever.) No case is known where materials conceivably present in wood, other than aldehydes, can react with phloroglucinol reagent, in the cold, to produce a red color. The colors formed with aniline and other amines, if caused by aldehydes, as is so apparent from the phloroglucinol results, are "aniles" (Schiff's bases).[1]

SPECTROSCOPIC STUDY OF COLORS PRODUCED BY "LIGNIN" REAGENTS

Some of the aldehyde in wood, which gives the "lignin" tests with phloroglucinol, pyrrole, and aniline, was obtained in benzene solution by the method of Czapek.[2] This method consists in boiling finely ground wood with stannous chloride solution, and extracting the wet mass with benzene for several days.

To some of this solution, diluted with alcohol, phloroglucinol, pyrrole, and *p*-nitroaniline reagents were added, and the characteristic cerise, dark red, and orange colors obtained were tested in a spectroscope. Solutions of (unpurified) eugenol and safrol, and pure cinnamic aldehyde, piperonal, vanillin, salicylaldehyde, anisaldehyde, and furfural were likewise treated with reagents and examined spectrometrically. (The compound with furfural changed color so rapidly it could not be measured.)

The phloroglucinol compounds of the wood-aldehyde, unpurified eugenol, unpurified safrol, vanillin, and salicylaldehyde, and the pyrrole compounds of the first three, gave more or less clear-cut bands of easy light transmission in the red and orange. In all the *p*-nitroaniline compounds, and the phloroglucinol and pyrrole compounds of the other aldehydes, the spectra were indefinite, and contained no well-marked bands, either of absorption or transmission. Using Formanek[1] units, the bands of highest transmission (minima of absorption) with phloroglucinol were at about 11.30 for wood, 11.30 for eugenol, 11.30 for safrol, 13.50 for vanillin, and 15.75 for salicylaldehyde. With pyrrole, the minimum absorption for wood aldehyde was at about 9.60 units; for eugenol and for safrol, at about 9.90 units. (In these three cases, the minima were not sharp, and might have been identical.)

The spectroscopic study indicates that oils of cloves and sassafras contain traces of a color-forming material very similar to, if not identical with, that in wood, with its probable origin in the woods from which these oils were distilled. Czapek's work and this spectroscopic work indicate that not more than a small fraction of the color-forming aldehyde of wood—Grafe[2] notwithstanding—can be vanillin,[3] although it might be *similar* to or decomposable into vanillin.[4]

The tinctorial power of phloroglucinol compounds is high, so that very slight traces of aldehyde suffice to produce strong colors. The amount in wood, as well as in oils of cloves and sassafras, is probably of the order of hundredths of a per cent.

COMBINATION OF ANILINE AND PHLOROGLUCINOL TESTS

Unpurified eugenol was diluted with 20 volumes of alcohol to serve as a reagent. This reagent was treated with aniline in hydrochloric acid, with immediate formation of a strong yellow color. When the eugenol reagent was treated with phloroglucinol in strong hydrochloric acid, a deep red color formed in less than 5 sec. When, now, some aniline solution was added to the eugenol reagent, followed by phloroglucinol, the red color did not appear strongly for nearly 60 sec.

Pine wood was treated with aniline plus hydrochloric acid, and the yellow-stained material dried. This treated wood and some plain wood were then treated with phloroglucinol solution in hydrochloric acid. The plain wood developed a red color in a few seconds, but the treated wood developed the color only after a minute.

Reversal of the test was next tried with eugenol. Phloroglucinol was first added, and when the color was at a maximum (about 15 min.), some aniline hydrochloride was added. A slight yellowing of the solution was noticeable on direct comparison with some of the solution to which the aniline salt had not been added.

These experiments and the one involving steam-distillation of eugenol from acid plus phloroglucinol mixture indicate that the material which causes the aniline test is also responsible for that with phloroglucinol. The aniline compound is formed at once, whereas that with phloroglucinol appears only after an appreciable lapse of time. Apparently the phloroglucinol and aniline divide the aldehyde between themselves in an equilibrium mixture, with the larger part going to the phloroglucinol.

The very excellent work by Czapek,[5] published in 1899, wherein he arrives at the conclusion that an aldehyde is present in wood which gives the color tests with phloroglucinol and the amines, is well borne out by these experiments. Czapek named the aldehyde "hadromal." He succeeded in concentrating it, but could not get it pure. Subsequent work by Grafe[6] seemed to show that hadromal was a mixture of vanillin, methyl furfural, and pyrocatechol. Czapek,[7] again, in turn, showed that no mixture of these three could duplicate the tests given by hadromal.

Very recently, Klason[8] has come to the conclusion that the principal color-forming aldehyde of wood is coniferyl aldehyde. The work in this laboratory, particularly the spectral analysis, points strongly to the soundness of Czapek's original work, and is entirely consistent with that of Klason. Up to the present, little success has attended the attempts of this laboratory to prepare coniferyl aldehyde from coniferin, so that it has not been possible to confirm Klason's work definitely by a comparison of the absorption spectra of the color tests.

---

[1] L. Zechmeister, "Kenntnis Cellulose und Lignins," Zurich, **1913**.

[2] *Z. physiol. Chem.*, **27** (1899), 141.

[1] "Spektral Analytische Nachweis," Berlin, **1900**.

[2] *Monatsh.*, **25** (1904), 987.

[3] Wichelhaus and Lange, *Ber.*, **49** (1916), 2001.

[4] M. Singer, *Monatsh.*, **3** (1882), 395.

[5] *Z. physiol. Chem.*, **27** (1899), 141.

[6] *Monatsh.*, **25** (1904), 987.

[7] "Biochemie der Pflanzen," Jena, **1913**.

[8] *Svensk Pappers-Tid.*, **23** (1920), 70; *C. A.*, **15** (1921), 526.

STUDY OF THE MÄULE REACTION

In 1900, Mäule[1] published the results of some experiments on wood, wherein he found that a bright red color often results when wood is treated, in succession, with neutral potassium permanganate solution, dilute hydrochloric acid, and finally ammonia. It has been noted in references to the Mäule reaction that pine wood gives a brown rather than red color, but so far as known, only one[2] clear-cut statement has been made regarding which kinds of woods do, and which do not, give the red color. This matter was, therefore, experimented upon, and some woods of uncommon botanical families, such as gingko, were tested.

Some eighteen species of deciduous woods, including the interesting balsa wood, eighteen species of coniferous woods, and gingko wood, were tested with Mäule reagent. All the woods of deciduous angiosperms gave distinct red colors. All those of coniferous gymnosperms, and of the deciduous gymnosperm, *Gingko biloba*, gave only indefinite yellow or pale brown colors.

The test is thus a convenient one for differentiating between the woods of angiosperms and those of gymnosperms. If gingko wood is excepted, the test distinguishes between deciduous and coniferous woods.

No woody fiber of cycads or other possible ancestors of the angiosperms was available for study. It would be very interesting, indeed, to determine if this reaction takes place with these now rare woods. If it does, the reaction would be a valuable tool in the hands of the botanist.

The reagents used were varied to determine the essential conditions and chemicals needed to produce the red color with "hard" woods. The results may be summarized as follows.

1—Potassium permanganate deposits manganese dioxide on the wood. This reacts with the hydrochloric acid to produce chlorine, which forms a compound which turns red with alkalis, in this case ammonia.

2—Chlorine water will replace permanganate and hydrochloric acid.

3—Bromine can replace chlorine, but the color in this case is a somewhat brownish red. Iodine will not produce the reaction.

4—Other oxidizing reagents, such as permanganate plus sulfuric acid (which deposits no manganese dioxide), do not give the red color.

5—Any alkali or organic base can replace ammonia, but usually not with advantage. Strong alkalis dissolve the color from the wood and thus weaken the test. Organic bases, and strong inorganic alkalis, give yellowish shades. Sodium bicarbonate can replace ammonia with the same deep red color, however.

6—Heat does not destroy the test at any part of the process, but reduces the sensitiveness at the last stage by dissolving color from the wood.

The Mäule test was applied to wood which had been extracted with various organic solvents, refluxed with acids, alkalis, and formaldehyde. The red color was given strongly. Jute, which was bleached nearly white with sodium peroxide, still gave a strong red color. Sulfate or soda-cooked, unbleached papers, however, gave no red color.

It is not improbable that the red color often obtained when chlorine-treated wood is treated with alkaline sodium sulfite, as in the Cross and Bevan method for cellulose determination, is a Mäule test.

The color-making material produced by chlorination is similar in nature to phenolphthalein, in that its acid form is light colored, and its salts deep red.

STUDY OF THE FERRICFERRICYANIDE TEST[1]

If a ferric chloride solution is added to a freshly prepared solution of potassium ferricyanide, a dark brown solution is obtained. This solution, when applied to wood, produces a deep green-blue color. Such a color is not given when the reagent is applied to filter paper. In this case, a diffuse pale blue is produced.

Some experiments have shown that this reaction is given by many other materials than wood. Any phenol or any amine gives the test. Inorganic reducing agents, such as stannous chloride, sulfurous acid, or hydrogen peroxide in acid solution also produce the green-blue color. (Certain aldehydes, as benzaldehyde and formaldehyde, do not give the test.)

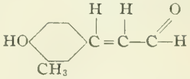
The fact that so many materials give the test makes its qualitative value as a *lignin* reagent very small.

CONCLUSIONS

1—Phloroglucinol, *p*-nitroaniline, and the other single-reagent color tests are not to be thought of as indicators of any appreciable part of the composition of lignin, but rather of traces of aldehyde which usually[2]—perhaps always—accompanies lignin.

2—All experiments, and particularly the spectroscopic work, are entirely consistent with the presence of one single color-producing aldehyde in wood, or, at least, the strong predominance of one aldehyde.

3—This aldehyde is not improbably coniferyl aldehyde,



as suggested very recently by the work of Klason.

4—Vanillin or furfural, if present, constitutes only a small fraction of the aldehyde content of the wood.

5—This work is in essential agreement with that of Czapek, who called the aldehyde of wood "hadromal."

6—Several of the nonaldehydic materials mentioned in the literature as giving color reactions similar to those of "lignin" have been shown to contain traces of aldehydes which are responsible for the color formation. In the cases of oils of cloves (eugenol) and sassafras (safrol) the aldehyde seems to be identical with that of wood, and is probably distilled from the wood along with the essential oils.

7—The Mäule reaction was found to consist essentially of a chlorination in acid solution of some compound in the wood, followed by alkaline treatment. A strong red color is developed in general in the case of deciduous woods, and only a weak indefinite brown color in the case of coniferous woods.

8—The Mäule reaction may prove valuable as a means of distinguishing between deciduous and coniferous woods, in mixtures of chips. It may, further, prove of interest to botanists, in tracing the ancestors of the present angiospermous trees, for the production of the reacting chemical is quite possibly inherited.

9—The ferric ferricyanide test (acting as it does in the presence of almost any reducing agent) is too general to be considered as a "lignin" reaction.

---

[1] *Fünfstücks, Beitr. Wiss. bot.*, **4** (1900), 166; also Habilitats Schrift, Stuttgart, **1901**.

[2] A. W. Schorger, THIS JOURNAL, **9** (1917), 561.

[1] R. Haller, *Färber-Ztg.*, **26** (1915), 157; *C. A.*, **10** (1916), 530.

[2] Cross, Bevan and Syndall, "Wood Pulp and Its Uses," London, **1911**.

The Calcium Chloride Method for the Determination of Water in Gasoline and in Certain Other Substances[1]

By Charles W. Clifford

Chemical Laboratories, Development Department, The Goodyear Tire and Rubber Co., Akron, Ohio

During an investigation in this laboratory it became desirable to obtain and verify, or to construct, the solubility curves for water in a certain gasoline and in benzene. This information is essential in many cases where a comparatively large change in temperature would cause separation of water from these solvents.

The only useful reference in the literature is to the work of E. Groschuff,[2] who determined solubilities of water in paraffin oil, kerosene, and benzene by heating and cooling definite amounts of the liquids with water in sealed tubes and noting the temperatures at which turbidity disappeared and reappeared. The original article was not available, but the two abstracts apparently covered all the essential points.

Investigation of Possible Methods for Determination of Water in Gasoline

With the procedure described above, the solubility is somewhat affected by change in pressure, and, therefore, the higher the temperature, the greater the pressure in the sealed tubes, and the more deviation from the true value at atmospheric pressure. Whether the solubility under pressure at a given temperature will be increased or decreased depends upon whether solution is accompanied by contraction or expansion in volume. The effect of the small pressure in these cases of very slight solubility was perhaps negligible, but with a gasoline having an initial boiling point around 40° C. the pressure might become an important factor. The application of this method would also present practical difficulties in sealing the tube, when applied to gasoline. Therefore it seemed desirable to determine solubilities of water in gasoline by some other method, and to compare the resulting values with those given for kerosene and paraffin oil.

Allen and Jacobs[3] enumerate ten methods for the determination of water in petroleum products. Only one of these (the method of Graefe[4] which consists of treatment with sodium and measurement of the evolved hydrogen) seemed accurate enough for this problem where such a small amount of water can be dissolved.

A study of other possibilities suggested a number of methods, including the following: (1) by calculation, based on the difference in specific gravities of the sample before and after dehydration; (2) by freezing out the water by immersion in a low-temperature bath; (3) by dilution with an oil dissolving much less water than gasoline; and (4) by selective absorption of water from the vaporized sample by some suitable reagent.

Method 1 has been shown by Graefe to be inaccurate for water in crude petroleum, and in the case of dissolved water in gasoline the difference in specific gravities would probably be less than one in the fourth decimal place. Method 2 is not a very practical one. Method 3 is difficult, since gasoline dissolves an extremely small amount of water, and is itself often used to precipitate water "quantitatively" from other organic liquids. Method 4 seemed worthy of trial, although no mention is made in the literature in regard to employing the most common dehydrators.

The most promising method, then, were:

1 The sodium method of Graefe.

2—Volatilization of the sample and absorption of the moisture in a dehydrating agent which would not absorb or react with the oil vapor.

Three 2.5-liter samples of this gasoline were secured at different times. The specific gravity was taken on the fresh sample with a pycnometer. All samples were kept securely stoppered in glass-stoppered bottles to avoid loss of the lighter fractions, and specific gravity determinations made on these samples from time to time gave constant values. This gasoline had a gravity of 0.70 (70° Bé.), and it was a "straight run" product. The initial boiling point was 40° C., and the "dry point" 145° C.

The Sodium Method

A constant-temperature bath was set up to maintain temperatures from 5° to 50° C., so that samples might be saturated with water at the desired temperatures. In testing the apparatus described by Allen and Jacobs[1] for the determination of water by treatment with sodium, it was found that 100 cc. of saturated gasoline would yield only 4 or 5 cc. of hydrogen, and that considerable time elapsed before the evolution was complete. Also, it was practically impossible to avoid some leakage during this time.

A simple one-piece apparatus was devised so that absolutely no leakage could occur, but here a vapor pressure correction became necessary. Attempts were made to determine the vapor pressure of this gasoline by the "barometer method,"[2] and results of from 168 mm. to 704 mm. Hg were obtained. Since gasoline is not a single chemical compound, but a mixture, its vapor pressure will vary with the boiling points of its constituents, the temperature, and the ratio of volume of sample to the space into which it can vaporize. Tubes of various heights filled with this gasoline alone also gave varying results. Calculation of the vapor pressure values[3] was not attempted. A table[4] of gasoline vapor pressure values is given in the literature, but the method of determination is not specified, and, since the boiling point of the gasoline quoted is considerably higher than that of this gasoline, the values for this gasoline could not be safely estimated.

The sodium method, therefore, was considered unsatisfactory for the determination of these small amounts of water in gasoline.

The Calcium Chloride Method

In the literature no mention is made of the ordinary drying agents, phosphoric anhydride, sulfuric acid, and anhydrous calcium chloride, although the use of plaster of Paris (both qualitatively[5] and quantitatively[6]) is given. It seemed reasonable to expect that calcium chloride, a practically neutral salt, might prove a satisfactory selective absorbent, while phosphoric anhydride and sulfuric acid might react with substances in the gasoline.

---

[1] Received September 23, 1920.

[2] *Elektrochem.*, **17** (1911), 348; *C. A.*, **5** (1911), 2550, *J. Chem. Soc.*, Abs., **100**, II, 595.

[3] Bureau of Mines, *Technical Paper* **25** (1912).

[4] *Petroleum*, **1** (1906), 813; *J. Soc. Chem. Ind.*, **25** (1906), 1035.

[1] *Loc. cit.*

[2] Holde-Mueller, "Examination of Hydrocarbon Oils," **1915**, 45.

[3] Williamson, "Pressure and Temperature Relations for Vapor of Liquids," *Chem. Met. Eng.*, **22** (1920), 1151.

[4] Olsen, Van Nostrand's "Chemical Annual," **1918**, 541.

[5] Allen, "Commercial Organic Analysis," **1915**, III, 116; cf. Lunge, "Coal Tar and Ammonia," **1909**, I, 320.

[6] Gill, "Oil Analysis," **1918**, 22; cf. Allen, "Commercial Organic Analysis," **1915**, I, 430.

QUALITATIVE TESTS—A very delicate test for water in gasoline was desired, in order that the portion of sample remaining after each trial run might be tested and the presence or absence of water ascertained. A comparison of three qualitative tests was made, with the results shown in Table I.

TABLE I—COMPARISON OF QUALITATIVE TESTS FOR WATER IN GASOLINE

Reagent	Sodium	$KMnO_4$	$AlCl_3$ (Anhyd.)
Indication of water	Evolution of H_2	Solution	Evolution of HCl
Gasoline dehydrated with Na	Negative	Negative	Negative
Gasoline, partly saturated	Positive	Negative	Negative
Gasoline, saturated	Positive	Negative	Negative

The qualitative test with sodium, therefore, is the only satisfactory one of the three enumerated.

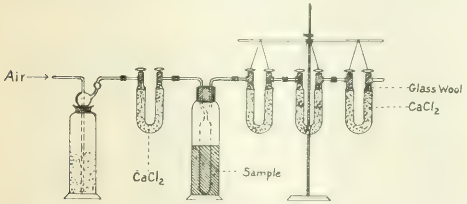


FIG. 1

PRELIMINARY TESTS—Tests were carried out in the apparatus shown in Fig. 1. Samples of water-saturated gasoline were volatilized with dry air, and the water was absorbed in the reagent contained in the U-tubes. The rate of air flow employed was 5 to 15 liters per hr. Separate tests were made with phosphoric anhydride, sulfuric acid, and calcium chloride; in each case the drying tower contained the same dehydrating agent as the absorption tubes.[1] The first U-tube after the drying tower merely protected the sample from foreign moisture. The absorption tubes filled with phosphoric anhydride, and especially those containing sulfuric acid, increased in weight out of all proportion to the dissolved water. The first tube containing calcium chloride showed a reasonable gain of a few milligrams, and the remaining gasoline from this trial run gave a negative test for water with metallic sodium. Further tests were made, therefore, with calcium chloride. This reagent was "C. P. anhydrous" in small lumps, produced by a reputable firm; it was crushed and screened rapidly, rejecting all except the portion from 10- to 20-mesh.

BLANK DETERMINATION ON GASOLINE—A sample of the gasoline was dehydrated with metallic sodium. About 39 g. of this anhydrous material were placed in a Vanier bulb, which was substituted for the larger gas-washing bottle employed in the previous tests. Air was passed through for about 2 hrs., then the Vanier bulb was removed, and dry air alone passed for over an hour. Table II summarizes the results obtained.

TABLE II—BLANK DETERMINATION ON GASOLINE DEHYDRATED WITH METALLIC SODIUM

No. of absorption tube[1]	1	2	3
Increase in weight, mg	0.9	0.7	0.9

[1] The tubes are numbered in the order shown in the sketch from left to right, excluding the tube which made certain that no moisture from the air passed through to the sample and following tubes. No data for this tube are given in these tables. It was weighed with the other three tubes. Its gain in weight was in most cases about 1 mg. or less.

The results show that the blank is small and fairly constant.

TEST FOR QUANTITATIVE RECOVERY OF ADDED WATER—The Vanier bulb containing anhydrous gasoline was next weighed, and reweighed after the addition of three drops of water from a 1-cc. pipet. The bulb was connected, and air was passed through. When the contents were shaken so as to suspend the water in fine droplets and allow good circulation, this water was apparently carried over in 0.5 hr. Without shaking, more time would have been required. Air was passed for 2 hrs., the bulb was removed, and dry air alone passed for 2 hrs. The results of this test appear in Table III.

TABLE III TEST OF QUANTITATIVE RECOVERY OF WATER ADDED TO ANHYDROUS GASOLINE

No. of absorption tube	1	2	3
Increase in weight, mg	62.2	1.0	0.6
Actual water added, mg	....	61.0	.
Water recovered, allowing blank of 0.6 mg	....	62.0	. .

The remaining portion of the gasoline sample was tested with metallic sodium, and water was found to be entirely absent. These results show that the water added was entirely recovered, and indicate that the method is accurate for water in gasoline. Solubility determinations with additional blanks (described in a following paper[1]) and later results furnish additional proof of the accuracy of this method. These results show that the water is entirely recovered in the first two absorption tubes, and that the first of these absorbs all except about 1 mg. The correct method of calculating results is found to be:

$$\frac{(\text{Increase, Tube 1} + \text{Increase, Tube 2}) - 2(\text{Blank})}{(\text{Volume of sample}) \times \text{Specific gravity}} = \text{per cent water by weight}$$

The dissolved or suspended water in any petroleum product can probably be determined satisfactorily by this calcium chloride method, first diluting the substance, if necessary, with anhydrous gasoline or kerosene.

APPLICATION OF THE CALCIUM CHLORIDE METHOD TO BENZENE—The accuracy of this method as applied to water in benzene was next investigated. This material was of the grade known as "100 per cent benzol," and when dehydrated had a specific gravity of 0.856 in air. The "dry point" was 80° to 82° C., and the liquid was clear and colorless. Blanks were run on both Na- and $CaCl_2$-dehydrated material. The average blank (from a total of 26 values) was 0.3 mg. Three tests for quantitative recovery of added water were made, and the results were as follows: 57.8 mg. taken, 56.9 mg. found; 44.0 mg. taken, 45.1 mg. found; 101.2 mg. taken, 101.8 mg. found. The remaining benzene from one run was again analyzed for water, and blank values were the result. The benzene remaining after each run was tested with metallic sodium, and water was entirely absent in each case. These results show that water in benzene can be accurately determined by this method.

EXTENSION OF METHOD TO WATER IN OTHER SUBSTANCES

The possible application of this method to other organic solvents and many solid substances offered an interesting field for investigation. If applicable, the method would furnish a ready means for determining large and small percentages of water and would preclude danger of decomposition, oxidation, or loss by vaporization which might occur upon heating.

Its accuracy was tested with some other liquids, using a Vanier bulb as a container in most cases. The method was also applied to a number of solid substances, using a gas-washing bottle as a container. Where convenient, tests were made with (*a*) samples of the solid alone, (*b*) samples suspended in a suitable tested medium (immiscible with water), and (*c*) samples dissolved in a suitable tested solvent (immiscible with water).

CHLOROFORM—The chloroform was of U. S. P. grade. After dehydration with $CaCl_2$, the specific gravity was 1.481 in air. The average blank was 1.2 mg. (average of eight values, including three from one run on a $CaCl_2$-dehydrated sample). With an anhydrous sample to which 38.0 mg. water had been added, 36.6 mg. were found upon analysis, and the water disappeared from the suspension in 0.5 hr. These results indicate that the method is accurate for water in chloroform.

---

[1] Fresenius-Cohn, "Quantitative Analysis," **1911**, II, 51.

[1] THIS JOURNAL, **13** (1921), 631.

CARBON TETRACHLORIDE—The sample was obtained by allowing the technical product to stand over sodium hydroxide, and then distilling over calcium chloride. It was clear, colorless, and neutral, and its specific gravity in air was about 1.60. The blank on this material was 0.6 mg. (average of six values, including those from one run on a $CaCl_2$-dehydrated sample). After 47.2 mg. of water had been added to an anhydrous sample, 48.2 mg. were found upon analysis. This method, then, is accurate for water in carbon tetrachloride.

CARBON BISULFIDE—This was obtained from technical material by one distillation over calcium chloride. It was clear and colorless, and had a specific gravity of 1.25 in air. The blank was 0 mg. (average of seventeen values, including those obtained with one test on a $CaCl_2$-dehydrated sample). 59.3 mg. of water were added to an anhydrous sample and upon analysis 60.3 mg. were found. The method is apparently satisfactory for water in carbon bisulfide.

ETHER—One test was made on U. S. P. ether saturated with water. The results indicated that the method is probably applicable to water in ether.

ACETONE—Technical acetone was distilled over calcium chloride. A portion of the distillate was shaken with fresh calcium chloride and allowed to stand several days, after which it was decanted, again shaken with calcium chloride, and allowed to stand. In these treatments the calcium chloride swelled to several times its original volume. When a sample of the clear supernatant acetone from the second dehydration was taken and an attempt made to obtain a blank by the calcium chloride method, the results showed that large amounts of acetone were held by the calcium chloride and that determination of water in acetone by this method is impossible.

PYRIDINE—When an attempt was made to dehydrate pyridine with calcium chloride, the latter swelled enormously. This was considered sufficient indication that pyridine would react with or be absorbed by the calcium chloride in the absorption tubes, and that the method was inapplicable.

ETHYL ALCOHOL—A test indicated that water cannot be removed quantitatively from ethyl alcohol by means of a current of dry air, as with gasoline. This test also indicated that the alcohol vapor is held to a certain extent by the calcium chloride in the absorption tubes, and that only after prolonged passage of dry air is the vapor displaced to a definite point. The calcium chloride method is therefore probably not applicable to water contained in alcohol.

GLYCEROL—One test run made with glycerol indicated that, as with alcohol, the water cannot be entirely removed in several hours by a current of dry air. This run, however, gave a small and constant blank. (Glycerol does not vaporize to an appreciable extent under these conditions.) The calcium chloride method is probably not applicable to the determination of water contained in glycerol.

CASTOR OIL—Castor oil was taken as a fairly typical oil of vegetable origin. One run with the oil dissolved in anhydrous benzene indicated that water in castor oil could probably be determined by this method.

SUCROSE—Two samples (one air-dry and the other moist) of granulated refined cane sugar were analyzed for water by the $CaCl_2$ method, using 10- to 15-g. portions. The actual moisture in each sample was determined by heating about 10 g. to constant weight (1.5 hrs.) in a ventilated electric oven at 105° C., and the duplicate values obtained agreed within 0.002 per cent with each sample. The only run made with the air-dry material checked within 0.001 per cent of the average value obtained by heating. Of three runs on the moist sucrose containing about 0.3 per cent water (with the sample alone, suspended in anhydrous benzene, and suspended in anhydrous carbon tetrachloride), the first result was within 0.002 per cent of the average value obtained by heating, the second was within 0.005 per cent, and the third checked this average value. With the sucrose taken alone, indications were that 0.5 hr. was sufficient to carry over all water. These results probably justify the conclusion that moisture in granulated sucrose can be accurately determined by the calcium chloride method.

ZINC OXIDE—The technical material intended for use as a pigment was employed. Results on two samples (taken alone, and suspended in anhydrous benzene) were much below the moisture values obtained by heating in the 105° C. oven to constant weight. The calcium chloride method, therefore, is not applicable.

CALCIUM CARBONATE—This was technical material intended for use as a pigment. Two samples were analyzed for moisture, one alone and the other suspended in anhydrous carbon tetrachloride. The results in both cases were only a fraction of the value obtained by heating at 105° C. to constant weight. The calcium chloride method is evidently not accurate for moisture in this pigment.

RUBBER STOCK—Small, freshly cut pieces of an uncured, reclaimed stock were weighed out. These pieces swelled but did not disintegrate when benzene, carbon bisulfide, carbon tetrachloride, or a mixture of these was added and a current of dry air passed through. The results obtained in these runs were very much lower than the value accepted as correct (obtained by heating samples for 2 hrs. at 105° C. in a very efficient vacuum dryer), and the calcium chloride method was considered inapplicable under these conditions.[1]

SULFUR—A test to determine moisture in flowers of sulfur was made, employing anhydrous carbon bisulfide as a solvent. The loss (0.034 per cent) after heating 4 hrs. at 70° C. was considered as representing the actual moisture present. The blank was small, but the results of this run showed no absorption of water. The calcium chloride method, therefore, cannot be considered applicable.

OXALIC ACID AND COPPER SULFATE—Tests on these substances in crystalline form would give some information as to whether water of crystallization can be determined by the calcium chloride method. Using materials of C. P. grade, the water was completely removed from the oxalic acid, while copper sulfate lost none. It seems from these results that air dried over calcium chloride may or may not remove water of crystallization in the time specified, depending upon the vapor pressure of the substance.

Description of Method

This method, then, is essentially as follows: A current of air previously dried by calcium chloride is passed through, or brought into intimate contact with, the sample at the rate of 5 to 15 liters per hr. for from 1 to 2 hrs. If a part of the water has settled out in the sample, it must be kept in suspension by frequent shaking, or by the current of air itself in order to secure complete vaporization in the time specified. The moisture abstracted from the sample by this air is absorbed in two calcium chloride tubes. If the sample is an appreciably volatile substance or is suspended or dissolved in such a substance, as gasoline, passage of a current of dry air direct from the calcium chloride tower at the rate of at least 5 liters per hour for at least 1 hr. is necessary in order to displace the vapor from the tubes before weighing. When the sample has an inappreciable vapor pressure and is taken alone, as sucrose, the tubes may be weighed immediately after absorption. A third $CaCl_2$ tube is advisable in order to secure a blank value for correction of results. Before each weighing, the tubes should be wiped carefully and allowed to reach the temperature of the balance. Suitable precautions should be taken to minimize introduction of air containing moisture, and the action of certain vapors on rubber connections. If, at the close of any run, there is doubt in regard to quantitative dehydration of the sample, the remaining portion may be analyzed again by this method, or a suitable qualitative test for water applied. The calculation of results is simple, and (for liquid samples) has been described above.

---

[1] The application of this method to moisture in pure unvulcanized gum (which can be readily dispersed in benzene or other solvents) was not investigated.

In all of these tests, where weighed amounts of water were added to liquids immiscible with water, the results show quantitative recovery within the limits of experimental error[1] (about 1 mg.). In tests where water was added to, and thoroughly suspended in, the liquid sample, it was noted that all water was apparently carried over in less than 0.5 hr.

The explanation of results obtained with all the liquids described lies in the law of partial pressures: In the cases where water was taken with an immiscible liquid, the vapor pressure of the water was the same as though the water existed alone, while in the cases where water was miscible in all proportions with the liquid, the water vapor pressure was markedly lowered and slow vaporization resulted. The small amount of alcohol in the chloroform used apparently did not affect the blank or the quantitative test. In the case of ether, which dissolves a comparatively large amount of water (the sample contained some alcohol also), the indications were nevertheless that this method could be successfully applied. Obviously, any suitable dehydrator might be substituted for calcium chloride in cases where the vapor of the sample would not react with, or be held by the dehydrator, and the method is applicable to moisture in gases when such a dehydrator is used.

SUMMARY

1—The sodium method is inapplicable to the determination of the small amounts of dissolved water in gasoline.

2—The calcium chloride method herein developed is accurate for the determination of water in gasoline, benzene, chloroform, carbon tetrachloride, and carbon bisulfide. Whether the water in these liquids is in solution or in suspension makes no difference in the accuracy of the method. The method should be accurate for water in any liquid with which it is entirely immiscible. It is probably accurate when applied to water in ether and in suitably diluted vegetable oils.

3—Acetone, pyridine, ethyl alcohol, and glycerol cannot be analyzed for water by the calcium chloride method. The first three, liquids which are miscible with water and appreciably volatile, are held to some extent by the calcium chloride and cannot be readily displaced. Ethyl alcohol and glycerol do not give up all contained water readily when dry air is passed through. The prediction may be safely made that this method will not be satisfactory for water contained in any liquid with which it is completely miscible.

4—The calcium chloride method is apparently accurate for moisture in granulated refined sugar (with the sample taken alone, or suspended in anhydrous benzene or carbon tetrachloride).

5—The method was unsuccessful when applied to moisture in the pigments examined (zinc oxide and calcium carbonate), in flowers of sulfur, and in a rubber stock.

6—Water of crystallization may or may not be accurately determined by this method, depending upon the vapor pressure of the compound.

The Solubility of Water in Gasoline and in Certain Other Organic Liquids, Determined by the Calcium Chloride Method[2]

By Charles W. Clifford

CHEMICAL LABORATORIES, DEVELOPMENT DEPARTMENT, THE GOODYEAR TIRE AND RUBBER CO., AKRON, OHIO

The actual solubility of water in the gasoline and in the benzene previously described[3] was sought, in order to determine the importance of this factor in a case where water appeared in cements containing these solvents. The calcium chloride method was employed for this determination.

SOLUBILITY OF WATER IN GASOLINE

The apparatus described in the preliminary tests of the method was used, and the air was passed successively through a gas-washing bottle, through a U-tube containing calcium chloride, through a gas-washing bottle containing the sample, and through three U-tubes filled with calcium chloride. After passing air from the compressed air line at the rate of 5 to 15 liters per hr. for about 1 hr., or until the U-tubes had attained constant weight, a 100-cc. sample of the saturated gasoline was carefully introduced and air again passed for 2 hrs., or until about one-fourth of the sample had been volatilized. The bottle containing the sample was then cut out and dry air passed for 1 hr. The tubes were then wiped thoroughly, allowed to reach the temperature of the balance, and weighed. Care was taken in manipulation that no air containing moisture was admitted into any piece of the apparatus, and where rubber connections were necessary as little surface as possible was exposed. The air from the last calcium chloride tube passed through a long glass tube which dipped under water, thus permitting the rate of air flow to be gaged approximately. Qualitative tests with metallic sodium on the remaining portions of several

TABLE I—SOLUBILITY OF WATER IN GASOLINE: SUMMARY OF RESULTS BY THE CALCIUM CHLORIDE METHOD

Saturation[1] Conditions Temp. °C.	Hours	Number of Run	Fraction[2] of Sample	Increase in Weight Milligrams Tube[3] 1	Tube 2	Tube 3	Grams Water per 100 Grams Solution
37.5	3.5	1	*a*	11.5	3.3	...	0.0175
37.5	3.5	1	*b*	1.7	2.4	...	......
37.5	3.5	1	*c*	2.6	2.5	...	......
37.5	3.5	1	*d*	—1.1	0.2	...	......
37.5	3.5	2	*a*	10.7	2.0	...	0.0145
37.5	3.5	2	*b*	1.8	3.2	...	......
37.5	3.5	2	*c*	2.6	2.1	...	......
37.5	3.5	2	*d*	—1.0	6.0	...	......
35.0	5	3	*a*	11.2	2.6	1.7	0.0161
35.0	5	4	*a*	10.0	1.0	...	0.0121
25.0	3	5	*a*	6.4	2.1	...	0.0085
25.0	3	5	*b*	0.0	1.0	...	......
25.0	3	6	*a*	7.1	3.1	...	0.0110
25.0	3	6	*b*	0.0	0.0	...	......
Dehydrated (Blank)		7	*a*	1.4	1.7	...	......
Dehydrated (Blank)		7	*b*	1.0	1.7	...	......
Dehydrated (Blank)		8	*a*	2.2	1.1	...	......
Dehydrated (Blank)		8	*b*	1.3	1.1	...	......
Dehydrated (Blank)		9	*a*	0.6	0.4	...	......
Dehydrated (Blank)		9	*b*	0.0	0.2	...	......
Dehydrated (Blank)		10	*a*	1.0	0.7	...	......
Dehydrated (Blank)		10	*b*	0.3	2.0	...	......

[1] It was noted that after thorough agitation, the time necessary for complete settling out of water from this gasoline varied from 0.7 hr. at 37.5° to more than 10 hrs. at 15°.

[2] These letters designate successive fractions of the 100-cc. sample volatilized by passing air for 2 hrs. (A test showed that for volatilizing successive *fourths* of the sample passage of air for approximately 2, 4, 7, and 20 hrs., respectively, were required.)

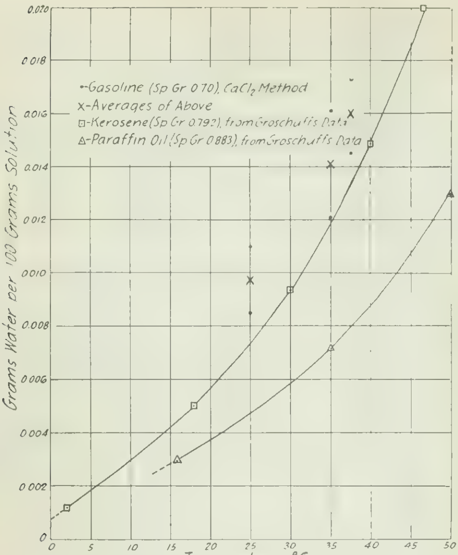
[3] The tubes are numbered in order, starting with that nearest the sample and excluding the tube which made certain that no moisture in the air passed through the drying tower to the sample and following tubes.

---

[1] The experimental work was limited by the amount of time available, but each test was very carefully performed.

[2] Received September 23, 1920.

[3] See preceding paper.



Solubility of Water in Petroleum Fractions

samples showed that water had been entirely removed. Table I summarizes the results obtained.

These results show that all the water is volatilized in the first fraction, which is about one-fourth of the sample. These and later data with other liquids show that this water is completely taken up in the first two absorption tubes and that the first of these absorbs all except about 1 mg. All increases in weight (except *a*, 1 and 2, where samples saturated with water were run) were averaged to obtain a blank. This average is 1.26 mg. The method of calculating results is:

$$\frac{(\text{Increase } a\ 1 + \text{Increase } a\ 2) - 2\ (\text{Blank})}{(\text{Volume of sample}) \times (\text{Specific gravity})} = \text{per cent water by weight}$$

All results by this method are plotted in the accompanying graph, and curves from Groschuff's data[1] for paraffin oil and kerosene are also included. These results by calcium chloride absorption agree for each temperature within about 25 per cent (about 0.003 per cent on the weight of sample).

They average about 0.002 per cent higher than Groschuff's kerosene values over this range of temperatures. We would expect the gasoline curve, representing another petroleum fraction, to resemble the curves for paraffin oil and kerosene. From the data obtained by the calcium chloride method it appears that the solubility curve for water in gasoline is similar to Groschuff's curves for kerosene and paraffin oil, and that the solubility of water in gasoline is somewhat greater than in kerosene. The experimental data are too limited to warrant any conclusion in regard to relation of solubility to specific gravity of the petroleum fraction.

Solubility of Water in Benzene and in Certain Other Liquids

The solubility of water in benzene, chloroform, carbon tetrachloride, and carbon bisulfide was next investigated by means of the calcium chloride method. This method[1] has been shown to be accurate for the determination of water in the above liquids. The samples of these four liquids used for solubility determinations were from the same lots as the samples with which the accuracy of the method was tested. The solubility values obtained appear in Table II.

Table II—Solubility of Water in Certain Organic Liquids (in Grams per 100 Grams Solution), Determined by the Calcium Chloride Method

		Benzene[1]		
Temperature, ° C	21.0	26.6	42.0	55.0
Solubility	0.046	0.056	0.088	0.113
		Chloroform		
Temperature., ° C	24.5	26.7	27.8	....
Solubility	0.084	0.107	0.116	....
	0.084	....	....	....
		Carbon Tetrachloride		
Temperature., ° C	24.0	28.5	....	....
Solubility	0.010	0.013	....	....
		Carbon Bisulfide		
Temperature, ° C	25.0	26.0	27.0	....
Solubility	0.010	0.011	0.012	....

[1] The benzene remaining after each run was tested with metallic sodium and water was entirely absent in each case. In one case the remaining benzene was again analyzed by this method before testing with sodium, and blank values were obtained.

The results show that an increase in solubility accompanies an increase in temperature, with each liquid. The values when plotted locate satisfactory solubility curves.

Summary

The solubility of water in gasoline, benzene, chloroform, carbon tetrachloride, and carbon bisulfide at various temperatures has been determined by the calcium chloride method and the values obtained have been presented.

Honors to Sir John Harrison

Among the honors which the King of England conferred upon distinguished scientists of his realm on his last birthday was the degree of Knighthood which was awarded to Professor J. B. Harrison, of Georgetown, Demerara. Professor Harrison has been a member of the American Chemical Society for twenty-seven years. An account of his chemical work as Director of Science and Agriculture in British Guiana was published in This Journal, **11** (1919), 874.

A. C. S. Monograph on "Glue and Gelatin"

In the preparation of the A. C. S. monograph on "Glue and Gelatin," Dr. Jerome Alexander is calling upon chemists and manufacturers for information of value, with a view to making the book as complete a resumé as possible of our present knowledge of the subject. Dr. Alexander would be glad to receive publications and reprints, as well as any information along historical, chemical, physical, and technical lines. Any communications should be addressed to Jerome Alexander, R. F. D. 4, Ridgefield, Conn.

A Grant for Research

The American Pharmaceutical Association has available about $360 to be expended after October 1, 1921, for the encouragement of research.

Investigators desiring financial aid in their work will communicate before September 1 with Prof. H. V. Arny, *chairman*, A. Ph. A. Research Committee, 115 West 68th St., New York, giving their past record and outlining the line of work for which the grant is desired.

---

[1] See preceding paper; also *Elektrochem.*, **17** (1911), 348; *C. A.*, **5** (1911), 2550; *J. Chem. Soc.*, Abs., **100** (1911), II, 595.

[1] See preceding paper.

Determination of the Volatile Matter in Graphite[1]

By Owen L. Shinn

Towne Scientific School, University of Pennsylvania, Philadelphia, Pa.

In the commercial analysis of graphite it frequently happens that dispute arises between two analysts as to the percentage of volatile matter in a given sample. In the present investigation this question was studied with the purpose of determining the cause of the different results obtained and of finding some remedy.

The literature contains very little upon this subject. The only recommendation to be found is to make the determination in the same manner as that used in determining the volatile matter in coal. This method consists in heating a sample for a definite time, in a closed platinum crucible, at a definite distance above a burner of definite size. The size of the burner, time of heating, placing of the crucible, etc., are the result of arbitrary selection, and the results are not accurate and are comparable only when obtained under exactly the same conditions. When this method of heating was applied to graphite, the results varied greatly. The variation of time by a few seconds introduced a large error. It was definitely noted that the variation was not proportional to the size of the sample, but was proportional to the time of heating, the burner used, or the temperature. These effects are plainly shown by the following results, obtained by heating 1-g. samples in a platinum crucible provided with a well-fitting lid. The crucible was the same in each case, but a good Bunsen burner and a 30-mm. Méker burner were used. The losses are given in per cent:

Time of heating, min	4	8	30
Over Bunsen burner	1.52	1.75	....
Over Méker burner	2.30	3.56	9.45

A method for the determination of the volatile matter in coke and anthracite coal, which has been in more or less general use for many years, is to heat the sample in an atmosphere of nitrogen. When 1-g. samples of the same lot of graphite as was used above were heated in nitrogen the losses were 0.88, 0.93, 0.94, and 0.94 per cent. The time of heating was 15, 30, 45, and 60 min., respectively. This shows that much of what was called volatile matter in the first tests was due to oxidation of part of the graphitic carbon.

Temperature of Heating

The first question to be answered was: At what temperature will the volatile matter be driven off when heated in nitrogen? Two methods of heating were tried: (*a*) a platinum boat in a silica tube, and (*b*) a Rose crucible. The first was found to be preferable. Below 400° C. the loss in weight was negligible, even though the heating was continued for over 2 hrs. A temperature of 600° C. was found to be sufficient, as no further loss was sustained by heating to a higher temperature. Heating samples to varying temperatures in a platinum crucible provided with a well-fitting lid gave the following results:

Temperature ° C.	Time Hours	Loss Per cent
150–170	1	0.05
250–270	1	0.11
300–325	1	0.11
400–450	1	0.31
450–500	1	3.34

This shows that below 450° C. the oxidation is very slight, but above that temperature carbon is burned off rapidly. It further shows that the volatile matter cannot be driven off at a temperature below that at which the carbon begins to oxidize. In order to reduce the percentage of oxidation the crucible was filled almost to the top with graphite, and heated for 8 min. The loss was 1.32 per cent. Attempts were made to drive the air out of the crucible by a layer of pure ammonium chloride, oxalic acid, or some organic substance which was non-coke-forming, but the values obtained were all about double that obtained by heating in nitrogen.

Time of Heating

As will be noted from the figures given above, the loss on heating in a closed crucible for 4 min. over a Méker burner is about three times that on heating in nitrogen. The time was reduced, until it was found that, by heating for exactly 30 sec. to a temperature of about 700° C., the loss in weight was just about equal to that obtained by heating in nitrogen. Five samples of a purified American graphite were heated in nitrogen to about 600° C. for 30 min., and the losses were 0.89, 0.85, 0.93, 0.91, and 0.90 per cent, or a mean of 0.896 per cent. Five other samples of the same substance were heated for exactly 30 sec. in a closed platinum crucible to about 700° C., and the losses were 0.95, 0.96, 0.99, 0.97, and 0.96 per cent, or a mean of 0.966 per cent. Similar samples heated under the same conditions for exactly 60 sec. gave the following results: 1.03, 1.02, 1.01, 1.04, and 0.99 per cent, or a mean of 1.018 per cent. The "coke" obtained from each of the samples heated for 30 sec. was further heated in nitrogen, and an additional loss of from 0.07 to 0.10 per cent was noted, showing that even in this short time of heating slight oxidation had taken place. The results obtained in this way were considered close enough for ordinary commercial determinations.

The same procedure was repeated with samples of commercial graphite from different localities, and the results obtained are noted in the following table:

Localities	Loss on Heating in Nitrogen Per cent	Loss on Heating for 30 Sec. in Closed Pt Crucible Per cent
Alabama	1.17	1.19–1.27
Connecticut	0.72	0.77–0.80
Canada	0.49	0.56–0.60
Madagascar	1.39	1.42–1.48
Norway	2.06	2.07–2.08
Ceylon (lump)	1.25	1.22–1.29
Ceylon (chip)	2.83	2.82–2.83

The problem under consideration seems to be quite analogous to that of determining the volatile matter in coke and anthracite coal. Mead and Attix[1] found that the factors noted above influenced their results. They claimed that the size of the crucible affected the amount of loss. A few isolated instances seemed to indicate this same influence in our experiments, but repeated attempts to prove this failed. Four crucibles holding 16, 17, 24, and 30 cc. were used. One-gram samples of three different graphites were heated in exactly the same way for 4 min., the losses being as follows:

Crucible			
1	1.52	1.16	2.88
2	1.53	1.22	2.79
3	1.43	1.18	2.75
4	1.43	1.20	2.85

The fit of the lid or the porosity of the platinum may have caused the variation, but evidently not the size of the crucibles, as they were all of the same relative shape and the surface exposed increased from 1 to 4, while the variation is not regular in that direction. In the analysis of coke and anthracite, Mead and Attix recommend heating for a certain time, weighing, heating for exactly the same time, and weighing again. They then consider the second loss oxidation, deduct a like amount from the first loss, and call the difference true volatile matter. This method was tried repeatedly with graphite, but the results were farther from the true value than when the sample was heated in a closed crucible for exactly 30 sec.

---

[1] Received March 10, 1921.

[1] *J. Am. Chem. Soc.*, **21** (1899), 1137.

The Nitrogen Method

From what has been said it is evident that any method of crucible heating by which air is in contact with the graphite is not accurate. The true value of the volatile matter in graphite can be determined only by heating in an atmosphere of pure nitrogen, hydrogen, or some other inert or nonreducible gas. This is best carried out by placing about a 1-g. sample in a platinum boat, and placing the boat in a silica tube through which a steady stream of pure nitrogen is passed. When the air has been completely expelled, the tube under the boat is heated for 30 min. with a 30-mm. Méker burner. It has been shown that 15 min. is long enough, but a half hour is recommended as a precaution. Various forms of heating and temperature control were tried, such as electric and gas heated combustion furnaces, electric tube furnace, multiple burners, etc., but the single Méker burner was found to be sufficient. It is important that pure nitrogen be used. Attempts to use commercial nitrogen containing 3.5 per cent of oxygen gave inaccurate results, the amount of loss depending upon the time of heating.

Substitute Method

The nitrogen method will consume over an hour and will require the preparation and purification of nitrogen, so that as a working method the following is suggested: Place a 1-g. sample of the graphite in a platinum crucible provided with a well-fitting lid. Support this in such a way that it can be heated to 700° to 750° C. (about 10 mm. above a good Méker burner), and heat for exactly 30 sec. As a method for the determination of volatile matter in coke and anthracite, the short heating process is entirely unsatisfactory.

Summary

1—It is pointed out that the method of determining volatile matter in graphite by heating in a crucible is rendered inaccurate by the oxidation of the graphite.

2—The error is dependent on the temperature, and time of heating, as well as on other factors.

3—The method of heating in a boat in an atmosphere of nitrogen gives accurate results, but is time-consuming, and requires pure nitrogen.

4—Results very close to the true value may be obtained by heating in a crucible in the air under certain stated conditions.

Discoloration in Canned Sweet Potatoes[1]

By **Edward F. Kohman**

Research Laboratory, National Canners Association, Washington, D. C.

The producer of canned foods must impart to his goods at least two prime and essential qualities before he can consider himself in any measure successful in his art. The first requisite is wholesomeness, secured by the sanitary packing of sound raw material when it is in that particular state of maturity most suitable for food. The second is palatability and appearance. On first thought it might seem that palatability and appearance are a necessary consequence of wholesomeness. This is not always the case, as is illustrated by various forms of discoloration in canned foods.

The discoloration in canned sweet potatoes is of this character. Sweet potatoes frequently become black in the can, unaccompanied by any other noticeable feature. Then discoloration apparently begins where the potatoes are in contact with the can, but may eventually permeate its entire contents. As there is usually a small amount of semiliquid starch paste in the bottom of the can, the discoloration is more pronounced there in the early stages, as the result of closer contact. How soon after packing discoloration sets in is a variable factor. From the experiments below, it would seem that in extreme cases it may occur very early.

All foods evolve hydrogen sulfide upon being heated. This sometimes leads to a black discoloration in canned foods, due to the formation of ferrous sulfide. From general appearance one cannot distinguish the discoloration of canned sweet potatoes from that due to the formation of ferrous sulfide, but a few qualitative tests sufficiently demonstrate its entirely different character. If black sweet potatoes are treated with dilute hydrochloric acid, the color is discharged, but when the acid is neutralized with ammonia, even after heating to drive out any hydrogen sulfide, the black color is again obtained. Hydrogen peroxide does not bleach the discolored sweet potatoes.

Effect of Air

Into a number of cans of sweet potatoes from each of two distinct commercial packs, both of which were normal in every way, air was admitted under sterile conditions by a very small puncture. The cans were placed in boiling water for some time to relieve the vacuum and thus to prevent the rapid inrush of air which would augment the chances of contamination. Alcohol was then burned on the top of the can. Just as the last had burned away, a puncture was made, and this was at once covered with a pad of sterilized cotton which was held in place by setting another can upon it. These cans were left undisturbed for periods of time ranging from a week to a month. At the end of a week, typical and distinct black discoloration of the sweet potatoes had set in in the bottom of the can, where there was the most moisture and the best contact between the can and its contents. This became more and more abundant as time elapsed. After varying periods of a week or more, some of the cans were resealed. These resealed cans retained the black that had formed in them to the end of the experiment. It could not be decided whether there was any increase of the black in the cans after resealing, because only a limited number of cans were used in the experiment.

This experiment makes very evident the necessity of air-tight seams in the cans. It does not answer the question as to the manner in which the admitted air brings about the discoloration, whether by direct action upon the sweet potatoes or by aiding the solution of the iron, which in turn is the immediate cause.

Effect of Iron Salts

To throw more light upon this point, sweet potatoes were canned with the addition of iron salts. The sweet potatoes were steamed in the usual way until soft, then peeled, and packed into No. 3 cans and into quart glass fruit jars. A varying amount of concentrated iron solution ranging from 100 mg. to 700 mg. per can was then added. It had already been found by analysis that black sweet potatoes contained amounts of iron as high as this. When this solution of iron was poured over the potatoes they immediately became black. Where a thick peel had been removed or where the ends were cut away, there was no appreciable darkening.

---

[1] Presented before the Division of Agricultural and Food Chemistry, at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

After processing, however, the entire potato was more or less permeated.

Effect of Peeling

This seemed to indicate that the substance that reacted with the iron to form the black compound was near the outer surface of the potato. Another lot was peeled rather thin in the raw state, as it was thought that the causative substance might permeate the entire potato during steaming. Then another moderately thick coat was peeled away. The potatoes and this second coat were steamed until tender and packed separately into glass jars, and iron was added to them as described above. The potatoes did not remain entirely free from discoloration, although it was very slight before processing and decidedly less after processing than with potatoes with only the usual amount of peel removed. The second coat that had been removed became very dark when iron was added.

That the troublesome substance was not all found near the outer surface was made clear by cutting raw sweet potatoes in cross-section and treating the cut surfaces with iron solution. Very soon a dark ring formed just inside the peel, and dark spots also appeared near the center. A region between the center and the outer portion remained almost free from discoloration. When the raw sweet potatoes were cut in cross-section a milky juice exuded in spots about the center. These spots were coincident with those where discoloration occurred when iron solution was applied.

Apparently the juice of the sweet potato contains a tannin-like substance which, in combination with iron, causes the discoloration. Any factor, such as a breathing can or a poor exhaust, which tends to hasten the solution of iron from the can, will augment discoloration. If no air is admitted into the can after sealing, any iron going into solution would be in the ferrous state. This does not form black compounds with tannins. Ferrous iron would very soon be oxidized upon opening the can, and it seems probable that the contents might then darken, but no such phenomenon has come under our observation.

Summary

The black discoloration in canned sweet potatoes is of a different character from that caused by the formation of ferrous sulfide in certain canned foods. It is the result of the combination of a tannin-like substance in the sweet potatoes with iron from the can. Since the production of this color with tannins requires iron in the ferric state, the access of air to the can is a prerequisite of its formation. The necessity of tight seams is therefore emphasized.

The substance which is involved in the discoloration is localized largely just under the peel. Since tannin probably permeates the potatoes to some extent during steaming, and since some is also found near the center of the potato, it does not seem possible to avoid this trouble by removing a thicker peel, either in the raw state or after steaming.

Composition of Hollyhock Seed and Oil [1,2]

By **R. S. Hiltner** and **L. Feldstein**

Denver Food and Drug Inspection Station, Bureau of Chemistry, U. S. Department of Agriculture, Denver, Colorado

The seeds of the hollyhock (*Althaea rosea*), as they mature on the stalks, are eaten by poultry, sparrows, and wild birds. Nothing can be found in the literature concerning the composition and food value of such seeds, or the character of the oil. As the hollyhock is a member of the mallow family (Malvaceae), it was thought possible that the oil from the seed might have qualities similar to those of cottonseed and kapok oils, which are derived from plants belonging to the same family.

The following was found to be the empirical composition of mature seeds threshed from pods of different varieties:

	Per cent
Moisture	4.4
Ash	6.9
Ether extract	11.9
Crude protein	21.2
Crude fiber	25.6
Starch	9.1

The ether extract was an oil with a greenish yellow color similar to that of raw linseed oil. The unrefined oil had at first a bland taste, but later developed an unpleasant bitter flavor. It showed the following properties:

Refractive index at 25° C.	1.4722
Specific gravity 15.6°/15.6°	0.9275
Iodine number	119.0
Halphen test	Positive
Bechi test	Positive

Like cottonseed oil, the hollyhock seed oil, after being heated for 10 min. at 250° C., no longer gave a color reaction with Halphen's reagent.

The most interesting point developed in this study was that the oil gave a strong, positive Halphen test, and also responded positively to Bechi's test. This fact is interesting for two reasons: It shows that the Halphen and Bechi tests are not distinctive of cottonseed oil exclusively, and it furnishes additional evidence in support of the view that the Halphen test is peculiar to the oils from the seeds of plants belonging to the mallow family[1] (Malvaceae) and the related bombax family (Bombaceae). Lewkowitsch[2] admits that the Halphen test cannot be considered as exclusively indicative of cottonseed oil, since kapok oil from *Bombax ceiba* or *Eriodendron anfractuosum* gives a similar color reaction.

So far as known, the chromogenic substance in cottonseed and kapok oils that gives the carmine color when heated with Halphen reagent has never been isolated or identified. Possibly the oils from the seeds of some of the other Malvaceae contain a larger amount of the chromogen, and a study of them might serve to reveal the identity of that substance. Members of this family which are commonly grown in this country are the okra (*Hibiscus* or *Abelmoschus esculentus*), the oil from the seeds of which has been recently described by Jamieson and Baughman;[3] the rose mallow (*Hibiscus moscheutos*); the shrubby althaea (*Hibiscus syriacus*); the musk mallow (*Malva moschata*); and the weeds, cheese mallow (*Malva rotundifolia*); and velvet mallow (*Abutilon theophrasti*).

It is doubtful if hollyhock oil will ever be an article of commerce, as the seed contains less than 13 per cent of oil, about half as much as is contained in cottonseed. On account of the quantity of ether extract and protein present, however, the seed might serve some useful purpose as a feedingstuff. While it is very light and bulky, individual plants seem to yield heavily, an average of about 100 g. of seed per plant being obtained from six plants.

---

[1] Received April 22, 1921.

[2] Published by permission of Secretary of Agriculture, U. S. Department of Agriculture.

[1] Ivanov and Kokotkina, "Physiological Characters of Plants and Botanical Families," Ivanov and Moshkova, "Data concerning the Character of Seeds of Different Varieties of Cotton," *C. A.*, **11** (1917), 2917.

[2] "Oils, Fats and Waxes," 3rd Ed., II, 534.

[3] *J. Am. Chem. Soc.*, **42** (1920), 166.

LABORATORY AND PLANT

A Modification of the Dumas Method, and the Application of the Kjeldahl Method to the Determination of Nitrogen in Nitronaphthalenes[1,2]

By **Paul H. M.-P. Brinton, F. M. Schertz, W. G. Crockett** and **P. P. Merkel**

School of Chemistry, University of Minnesota, St. Paul, Minn.

In carrying out nitration investigations in connection with nitronaphthalenes it is necessary to make frequent determinations of nitrogen. Unfortunately, the convenient method of Kjeldahl has been found to give low results when applied to nitronaphthalenes, and it has been necessary to have recourse to the method of Dumas, which requires constant attention, and unusual care in execution if the results are to be reliable.

The investigation here recorded had as its aim the determination of the relative values for nitrogen in typical nitronaphthalenes by a modified Dumas method; the Kjeldahl method, as modified by Jodlbauer, Gunning, and others;[3] and the phosphorus iodide method,[4] which is also a modification of the Kjeldahl process. Five samples of nitronaphthalenes, which we supposed to be typical of the more highly nitrated mixtures likely to be met in the nitration tests, were prepared with every precaution to secure uniformity in the individual lots, and were analyzed by the three procedures.

The Dumas Method

The Dumas method has long been recognized as a standard one for the determination of nitrogen in the vast majority of nitrogenous organic substances, and is conceded to be accurate if carried out with all the necessary precautions. There are so many sources of error, however, and the manipulations require such unusual attention to details that it is not suited to routine control work. In the present investigation every effort was made to eliminate sources of error, and a procedure was finally developed by which concordant results were obtained on certain pure standards. The procedure and apparatus are not held to be the simplest possible for the attainment of accurate results, but this combination does yield the accuracy desired, and for the present purpose it was not considered necessary to strive for greater simplicity.

Apparatus

The apparatus, as developed mainly by F. M. Schertz, is shown in the accompanying cut, in which the various items are not drawn to scale, and from which all parts of the apparatus not necessary to the understanding of the process (such as furnace, supports, etc.) are omitted.

Generator—On the floor under the table a heavy 20-liter glass bottle serves as the carbon dioxide generating chamber. On a shelf 8 ft. above the generator are two 10-liter bottles, containing saturated sodium carbonate solution and 1 : 1 sulfuric acid, respectively. These bottles are connected with the generator bottle as shown in the cut. It is essential that the stopcocks, *a* and *b*, of these feed bottles be located at the low level shown, and not close to the feed bottles, since the latter arrangement would cause a back pressure of CO_2 in the feed tubes, sufficient to prevent the flow of liquid. A drop of about 8 ft. is required to establish the pressure necessary for the whole system. The stopper of the generator bottle carries three tubes: one the common outlet of the forked feed tubes, one the delivery tube to the measuring bottles, and one the drain tube, which reaches to the bottom of the chamber and carries the stopcock, *c*.

The big generator bottle is completely filled with boiled and cooled water, the tubes leading from the feed bottles are filled with their respective solutions, and the stopper of the generator is firmly inserted and made entirely tight with sealing wax.

Measuring Bottles—Two bottles, R and S, of 2.5-liter capacity are each fitted with three-hole stoppers, through which pass three tubes connecting the two bottles. The first of these tubes is a long siphon reaching to the bottom of each bottle. The other two tubes end just below the stoppers, and each of these two tubes has a 3-way stopcock in the center. The stopcock *g* connects with the generator through tube *d*, and stopcock *f* connects with the furnace through tube *n*. Before inserting the stoppers into these bottles, one of them (say, S) is filled nearly full of cold, recently boiled water. The level of the water should be about an inch below the ends of the tubes which terminate just under the stoppers. The stoppers are inserted and fixed in place with sealing wax.

A U-tube is inserted between the measuring bottles and the furnace in the position shown, to prevent the excessive passage of water into the combustion tube.

Absorption System—Three Schiff nitrometers are connected as shown in the illustration. It will be seen that by manipulation of the two 3-way stopcocks, *u* and *y*, it is possible to connect any one of the nitrometers with any other, or with the outer air through the tube leading into the drain bottle E. Nitrometer II is encased in a water jacket with a thermometer, for more exact control of volume when reading. This nitrometer is accurately calibrated. The others need not be. The regular gas inlet arms of nitrometers II and III are closed, as they are not needed. No mercury is required in these two nitrometers, but in I such an amount of mercury is added that its surface shall come about half way between the inlet arm and the leveling bulb arm. All gases coming from the combustion tube enter the absorption system through nitrometer I. Bulb D is inserted between leveling bulb A (which functions as a permanent reservoir) and nitrometer I, to act as a trap for any air which might be mechanically carried down into the nitrometer on pouring caustic solution into A, as well as for any small amount of nitrogen that might find its way into the leveling arm. By adjusting the relative positions of A and D, the trapped air or nitrogen can be expelled through A or returned to the nitrometer as the case may demand.

DETAILS OF OPERATION—*Removal of Air*—The big generator bottle being completely filled with water and the stopper sealed in as before described, all connections are made as shown in the cut. Stopcock *c* is opened and a little acid is admitted through cock *b*, a little water running out through cock *c* to make room for the acid. Cock *b* is closed, and a little sodium carbonate solution is than admitted through *a*. Any air in *d* and in the top of the generator bottle is blown out through *d* by the carbon dioxide generated, and then the 3-way cock, *g*, is closed, whereupon water is forced out through the open cock, *c*, until the generator contains only pure carbon dioxide. Cock *c* is now closed, and *b* is opened, allowing about a liter of the acid to run into the generator. The carbonate solution

---

[1] Received March 31, 1921.

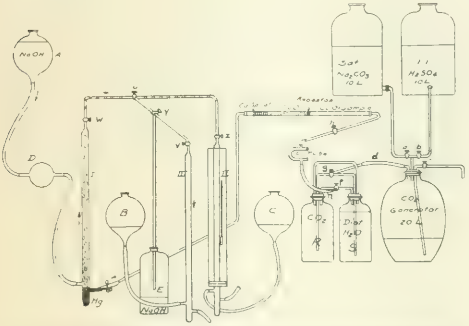
[2] Published by permission of the Chief of Chemical Warfare Service, U. S. Army.

[3] Marshall, "Explosives," II, 731.

[4] Cope and Taylor, Bureau of Mines, *Technical Paper* **160**.

is now let in until no more will flow because of the pressure of the carbon dioxide in the generator.

Stopcock *g* is now adjusted so that carbon dioxide flows from the generator into the bottle S, which forces the water from that bottle through the siphon into bottle R, while the air from R is forced out through *n* by properly adjusting stopcock *f*. When all the water from S has passed into R, cocks *g* and *f* are adjusted so that carbon dioxide from the generator flows into R, forcing the water back through the siphon into S, while the carbon dioxide from S is forced into the combustion tube through *n*. By repeating these operations a few times, and admitting sodium carbonate solution to the generator as needed, the generator, measuring bottles, connecting tubes, and combustion tube will be freed from original air and will contain only carbon dioxide of the grade furnished by the generator, which, however, contains a very slight amount of air—hence the necessity of the measuring bottles.



Apparatus for the Determination of Nitrogen in Nitronaphthalene by Dumas Method

It is, of course, not necessary to go through this whole operation before every analysis, for if the train be kept closed, air is not admitted to any part of the generating system, and only the combustion tube and nitrometers must be cleared before each run. The sealed stoppers of the generator and measuring bottles need never be removed, as the spent liquor is run out of the generator by the long siphon tube.

The Combustion Tube—The hard Pyrex glass combustion tube is wrapped with asbestos paper and over this is wound iron wire. This prevents bulging, and prolongs the life of the tube greatly. The copper oxide is prepared by long ignition in nickel crucibles, and preserved in stoppered bottles, with the usual precautions.

In the middle of the tube is placed a plug of ignited asbestos, about 1 in. long, and the half of the tube toward the nitrometer side is filled with coarse copper oxide and the reduced copper spiral in the conventional way. On the other side of the asbestos plug a short layer (an inch or two) of medium grade copper oxide is placed, and after this the intimate mixture of sample and fine copper oxide. It has been found desirable to dilute the sample quite freely with copper oxide, so that the layer containing the sample is from 5 to 7 in. long. Behind this comes an oxidized copper spiral.

The Combustion—In starting the run, the charged tube is heated by lighting the burners under it from the end nearest the nitrometers to within about 3 in. of the asbestos plug, at the same time passing a brisk current of carbon dioxide through the tube. A damp towel is laid over the part of the tube containing the sample to guard against prematurely liberating nitrogen. About one measuring bottle of carbon dioxide is passed through the tube to clear the system of air. This gas passes into nitrometer I, in which the level of the hydroxide solution is held just a little above the side arms by suitably lowering A and D. Stopcocks *w*, *u*, and *y* are adjusted so that the gas passes out through drain bottle E. After the passage of this bottle of carbon dioxide, the nitrometers and connecting tubes are completely filled with sodium hydroxide by manipulating the stopcocks and leveling bulbs. Exactly one bottle of carbon dioxide is now run as a blank. This gas, after passing through the furnace, enters nitrometer I at the bottom, and passes over into nitrometer II through the open stopcocks *w*, *u*, and *z*. (*u* is so set that nitrometers I and II are connected, but III is cut out.) At the start A and D are at about the relative levels shown in the cut. It is evident that there will be a gradual flow of sodium hydroxide solution from A to C, passing up through nitrometer I and down through Nitrometer II. There is thus a current of solution going along with the gas, and this greatly facilitates absorption. When the supply of sodium hydroxide in A becomes small, and that in C large, liquid from C is poured into a beaker and transferred to A. Any air will collect in the upper part of nitrometer II, and when the one bottleful of carbon dioxide has been passed through the system, stopcock *h*, between the measuring bottle and the furnace, is closed. Any small bubbles of gas in the upper part of nitrometer I, in the connecting tube between *w* and *z*, and in the upper part of nitrometer II, are collected in nitrometer II, and the cocks *w* and *z* are closed. The small volume of gas is read off in the conventional way, bringing the level of the liquid in C to coincide with the liquid surface in the nitrometer. This volume gives the blank for one bottleful of carbon dioxide, and in our experience it has been usually of the order of 1 cc. or less. If the generator has stood for some time the blank runs a little higher than when the generator is in more constant use. The little volume of air is expelled through *z*, *u*, *y*, and out through drain bottle E.

The combustion of the sample is now begun by opening stopcock *h* and allowing a very slow current of carbon dioxide to pass through the tube, *w*, *u*, and *z* being adjusted to permit the circulation just as they were in running the blank. Two or three burners are lighted at the extreme end nearest the generator, and at the same time two more burners are ignited under the coarse copper oxide, thus making the heated area extend from the reduced copper spiral to the asbestos plug in the center of the tube. The damp cloth is removed from over the center, and the sample is burned by very gradually heating from both sides. It must be strongly emphasized that the evolution of nitrogen must be gradual. During the combustion half a bottle (about 1.25 liters) of carbon dioxide are used, and a bottle and a half (3.75 liters) are used to sweep out all nitrogen. When most of the nitrogen has passed into the nitrometers, the rate of flow of the carbon dioxide is increased to a brisk stream.

For greater accuracy, large samples (about 1.5 g.) have been used, and this has necessitated the use of the third nitrometer. When nitrometer II becomes nearly full of nitrogen, the current of gas is deflected into nitrometer III by manipulating the 3-way cocks, *u* and *y*, and opening cock *v*. The current of gas is now up through nitrometer I, turning at *u*, passing through, and down into nitrometer III, where it collects. The flow of absorbent liquid is now down from A, up through nitrometer I, down through nitrometer II, and into leveling bulb B, from which it is transferred back to A when necessary, by means of a beaker.

After standing half an hour in the water-jacketed nitrometer II, the volume of nitrogen is carefully read, and then passed out through *z*, *u*, and *y*, into the drain bottle E. The nitrogen from nitrometer III is now transferred to the water-jacketed nitrometer, and its volume is read in the same way.

A complete run requires an hour and a half. When the run is finished the heat is turned off, the pinchcock at the inlet of nitrometer I is closed, and the furnace is allowed to cool under a slight pressure of carbon dioxide. The generator is then closed by turning cocks *g* and *f* between the measuring bottles to neutral positions.

Results—A large number of preliminary analyses were run both on the nitronaphthalenes and on specially purified nitro compounds; and the results of these runs were used in developing details of the method. After the method was developed three consecutive runs on each of the five samples were made, and the percentages of nitrogen found, without omission of any figures, are given in Table I.

TABLE I

SAMPLE	1	2	3	4	5
	14.31	14.65	14.89	16.10	16.91
	14.39	14.47	14.97	16.15	16.89
	14.28	14.71	14.93	16.19	16.74
AVERAGE	14.33	14.61	14.93	16.15	16.85

Just before, just after, and interspersed with these determinations, samples of specially purified picric acid and dinitrobenzene were run as checks on the accuracy of the operations. The following results were obtained.

	PICRIC ACID	DINITROBENZENE
	18.39	16.78
	18.46	16.61
	18.49	16.69
AVERAGE	18.45 Per cent Nitrogen	16.70 Per cent Nitrogen
THEORY	18.35 Per cent Nitrogen	16.64 Per cent Nitrogen

THE KJELDAHL-GUNNING-JODLBAUER METHOD

OUTLINE OF METHOD—A sample of about 0.5 g. is weighed into a 500-cc. Kjeldahl flask. (Convenient for this purpose is a spoon made from a rather heavy glass rod 15 in. long, by heating and molding one end to a spoon shape. The sample is dipped carefully from a weighed bottle, and transferred to the bottom of the flask, the spoon bowl being brushed off with a short bristled camel's brush, which has been cut off at its head and tied with fine copper wire to the short arm of a right-angled glass rod, the two arms of which measure 18 in. and 0.25 in., respectively. The bottle is again weighed, and the weight of the sample is obtained by difference. The brush must be a good one, with no loose hairs that might stay in the flask and raise the nitrogen content.) Thirty cc. of strong sulfuric acid, containing 2 g. of salicylic acid, are poured rapidly over the sample, and the flask is rotated and set on the steam bath. Most nitronaphthalenes will completely dissolve, and this should be attained if possible. Some samples, very high in nitrogen, will not give a clear solution, and a muddy residue remains even after many hours on the steam bath. With such a sample it has been found sufficient to heat for 2 hrs. with occasional agitation, and to proceed in spite of the muddy residue. After cooling, 2 g. of zinc dust are added in small portions, to avoid local heating. The flask is shaken occasionally for an hour or two, and allowed to stand over night. Next morning it is heated in a water bath for an hour at 70°, and then over a small flame until all visible action is over. After cooling somewhat, 1 g. of mercury or mercuric oxide is added, and the contents of the flask are gently boiled for 1 or 1.5 hrs. After cooling, 7.5 g. of potassium sulfate are added, and the boiling is continued for 1 or 1.5 hrs. The flask is cooled and 250 cc. of water are added to dissolve the cake, after which 25 cc. of 8 per cent sodium sulfide solution and 1 g. of granulated zinc are added. Ninety cc. of sodium hydroxide solution (750 g. to 1 liter of water), or enough to make the solution strongly alkaline, are poured into the flask, the latter is immediately connected with the condenser, and the ammonia is distilled off into standard acid, and titrated in the usual way.

In Table II are shown the percentages of nitrogen found in the five samples by this method.

TABLE II

SAMPLE	1	2	3	4	5
	13.74	13.93	14.20	14.93	15.55
	13.85	13.[illegible]	14.10	15.16	15.61
	13.67	13.84	14.17	14.91	15.41
	.....	14.01	14.07	.....	15.35
AVERAGE	13.74	13.94	14.14	15.00	15.48

THE PHOSPHORUS IODIDE METHOD

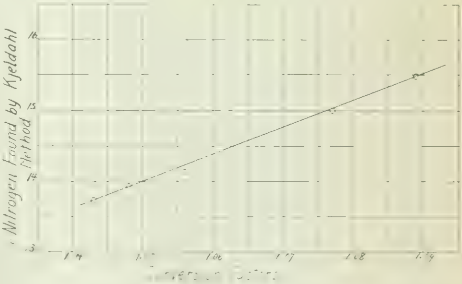
This method was carried out according to the details quoted by Cope and Taylor, and specific directions need not be given here. In Table III the percentages of nitrogen found by this method are shown.

TABLE III

SAMPLE	1	2	3	4	5
	13.94	13.61	14.05	15.22	16.27
	13.54	13.46	13.88	15.05	16.24
	13.49	13.85	14.24	15.13	16.12
	13.67	13.74	13.99	15.12	16.10
	13.92	13.64	13.83	15.03	16.02
	13.91	13.82	13.95	.....	.....
	13.73	.....	13.83	.....	.....
	13.81	.....	.....	.....	.....
AVERAGE	13.75	13.69	13.97	15.11	16.15

COMPARISON OF RESULTS BY THE THREE METHODS

The phosphorus iodide method was not found satisfactory in its present form, and the high cost of reagents did not encourage us to pursue work on the process. The addition of water to the phosphorus iodide occasionally causes annoying, although not dangerous, explosions. On some samples the results by this method are higher, and on some samples lower, than those by the other modifications of the Kjeldahl method.



An interesting relationship between the results obtained by the Dumas and the Kjeldahl-Gunning-Jodlbauer methods was found. In Table IV is shown a comparison of the average values found by these two methods, the last line of the table giving the ratios obtained by dividing the percentage nitrogen found by the Dumas method by that found by the modified Kjeldahl method.

TABLE IV

SAMPLE	1	2	3	4	5
Per cent N by Dumas method	14.33	14.61	14.93	16.15	16.85
Per cent N by modified Kjeldahl method	13.74	13.94	14.14	15.00	15.48
RATIO	1.043	1.048	1.056	1.077	1.089

In the accompanying graph these ratios are plotted as abscissas against the percentages of nitrogen found by the modified Kjeldahl method as ordinates. It will be seen that the ratio is a linear function of the nitrogen content; and the determined points fall sufficiently close to the straight line to allow the true nitrogen content of a nitronaphthalene to be calculated with a surprising degree of accuracy from a determination by the Kjeldahl-Gunning-Jodlbauer method.

As an example, let us assume that 14.55 per cent nitrogen were found by the modified Kjeldahl method. The conversion factor corresponding to this percentage is found from the graph to be 1.064. Then 14.55 multiplied by 1.064 gives 15.48 per cent as the true nitrogen content of the sample of nitronaphthalene.

SUMMARY

A modification of the Dumas method for determination of the nitrogen in organic substances has been worked out for use with compounds of high nitrogen content, and with sodium hydroxide in place of potassium hydroxide as the absorbing agent.

The various modifications of the Kjeldahl method having been found to give low results when applied to the determination of nitrogen in mixed nitronaphthalenes, a study of the exact degrees of variation between the true nitrogen content, as shown by the Dumas method, and the apparent nitrogen content shown by the Kjeldahl-Gunning-Jodlbauer method has been made.

The degree of variation has been found to increase as a linear function of the nitrogen content, and a series of conversion factors has been plotted, which allows the convenient Kjeldahl-Gunning-Jodlbauer method to be used in the technical control of the nitration of naphthalene. The true percentage of nitrogen is found by multiplying the percentage found by the modified Kjeldahl method by the corresponding conversion factor.

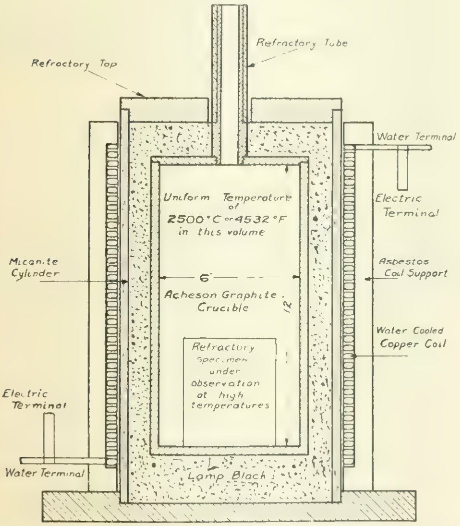
Uniform High Temperature throughout a Large Volume[1]

By **E. F. Northrup**

AJAX ELECTROTHERMIC CORPORATION, TRENTON, NEW JERSEY

The writer wishes to call attention to the possibilities now made commercially available of heating a space of considerable volume to temperatures exceeding 2000° C., the temperature being absolutely uniform throughout the space.

A heated chamber of this character can be used to the very best advantage for determining the properties of commercial refractories, or for the firing at high temperatures of ceramic materials, such as the spark plugs used in gasoline engines.



The result sought is obtained by the device shown in the figure. A crucible is turned up out of an electrode made of Acheson graphite, the wall of the crucible being about 0.375 in., the interior diameter being 6 in., and the depth 12 in. The crucible is fitted with a graphite cover also about 0.375 in. thick. Screwed into the cover at its center is a tube of graphite which extends a foot or more above the cover. The hole through this tube serves as a sight hole for optically determining the temperature. This crucible is located in a cylinder made of micanite. It is packed about with lampblack, the lampblack being beneath the bottom and piled over the top of the cover of the crucible. On the outside of the micanite cylinder is a water-cooled coil of about fifty turns of flattened copper tubing. Water obtained from the supply mains flows through this coil and maintains the coil near room temperature at all times. High frequency voltage (10,000 to 20,000 cycles) is applied at the terminals of the coil, which carries from 60 to 100 amperes of high frequency current. This current is readily supplied by a high frequency converter operated at 20 k. w.

In this case the lampblack, which is a semielectrical insulator, serves as a heat insulator. The heat insulation of lampblack at temperatures around 2000° C. is probably better than that of any other known material.

Under the above conditions the interior of the crucible attains within less than an hour a temperature of 2000° C., and can even be pushed up to 2500° C., and this temperature is, as nearly as optical means can determine, exactly the same throughout the interior of the crucible. There is no other device, so far as the writer is aware, which will heat a space of one-fifth cubic foot, or so, uniformly to this high temperature and in so short a time.

This arrangement is one of the simplest and most effective applications of high frequency current to heating. Problems connected with the heat treatment of refractories, or the graphitization of small pieces of carbon are studied with great ease and at uniform temperatures higher than have heretofore been made available by any other type of electric furnace. The temperature is furthermore under the most perfect control, and can be varied in the simplest manner in infinitesimal steps.

If it is desired to study the crushing strength of refractories when brought to very high temperatures, it is easy to produce the pressure on the refractory piece set in the bottom of the crucible by means of a graphite rod passed through a hole in the cover of the crucible.

If the problem requires the heating of a larger chamber than that shown in the figure, say, a chamber of the capacity of 1 cu. ft., the same results can be obtained by energizing the inductor coil with high frequency current obtained from a converter of greater power, converters rated at 60 k. w. now being commercially available.

During the month of June 1921, eighteen companies were organized in the field of chemicals, drugs, and dyes, with an aggregate capitalization of $3,325,000, which is the smallest reported for any month in 1920 and 1921. The authorized capitalization for the six months ending June 1921 was $65,625,000, as compared with $109,731,500 for the first six months of 1920. The second quarter of 1921 falls considerably below the record for the first quarter, the comparative figures being $25,115,000 and $40,510,000. The following table shows the development of drug and chemical concerns since August 1914:

Five months 1914	$ 16,838,000
Year 1915	65,565,000
1916	99,244,000
1917	146,160,000
1918	73,403,000
1919	112,173,000
1920	487,148,900
Six months 1921	65,625,000

---

[1] Received April 28, 1921.

A Rotary Digester for Use in Bagasse Analysis[1]

By Guilford L. Spencer

The Cuban-American Sugar Company, New York, N. Y.

The determination of sugar in cane bagasse, with the customary digesters, usually presents difficulties through the need of keeping the material in motion while treating it with hot water. Motion is necessary to promote maceration and diffusion. Following the digestion, the extract must be cooled and, without special arrangement, this is a slow process. Further, many bagasse tests must be made daily in full control of cane milling. To permit attention to other duties, the chemist must be relieved of as much of the immediate supervision of the bagasse tests as is possible.

To facilitate this testing, the author has devised a rotary digester, which is simply a steam bath in which cylinders, containing the sample and water, are rotated. The apparatus is fitted for three simultaneous tests. The casing of the digester is cylindrical and of 24-in. internal diameter. A triangular hub, 4 in. long, turns freely with a shaft, which is fitted with an adjustable cone bearing inside the digester casing at one end, while the other end projects through a bronze bearing and carries a pulley 18 in. in diameter. The pulley is grooved for a sewing machine belt or a light chain. Clamps are provided on the hub for attaching three aluminium cylinders, 4 in. in diameter by 8 in. long, for samples. The clamps also hold the covers of the cylinders in position. The covers have break-vacuum cocks. The pulley is connected through a laboratory reducing gear, 48 : 1, with a small electric motor, and is rotated at about 5 r. p. m. The cylinders are revolved endwise. A hinged cover closes the apparatus when in use. The casing is drained by a 1-in. pipe, provided with a stop valve. A 1-in. overflow pipe leads from a point below the shaft and connects with the drain below the stop valve. The apparatus is provided with a 0.125-in. steam pipe and a 0.5-in. cold water pipe.

The following is the procedure in making a sugar test with this digester: 100 g. of chopped bagasse are weighed in a tared cylinder; 1 liter of very hot water is added; the cover, with the cock closed, is placed in position on the cylinder and this is then locked on the hub. If ammonia is used in preserving the material while collecting the sample, no alkali is added to the digestion water; otherwise sodium carbonate is added. The cover is closed, and with the bottom drain open steam is turned into the casing. Very little steam is needed. With the outlet to the drain open, the pressure is that of the atmosphere. The cylinders are revolved for an hour in the steam and this is then shut off, and the drain is closed; cold water is now admitted and the revolution of the hub is continued until the sample is cooled. The drain is opened, and the cylinder is removed, dried, and weighed. Further procedure is as in the customary methods of analysis.

As may be noted, the slow motion of the hub causes the bagasse to fall from end to end of the cylinder, agitates the extract, and promotes maceration and diffusion.

Continuous Sampling of Sugar Liquors[1]

By Walter L. Jordan

83 Washington Place, New York, N. Y.

Sampling of sugar juices and liquors is of first importance in mill and refinery control. Exact analytical work in the laboratory will have little value if the samples do not truly represent the products that are going through the mill or factory.

Usually samples are taken periodically. The men at the various stations are given bottles to be filled at intervals of 1 or 2 hrs. The sample is dependent upon the sampler, and he soon learns to take samples that show his own work to be satisfactory, instead of those that will correctly reflect manufacturing conditions and assist in the process control.

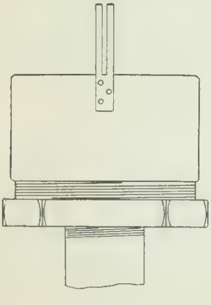


Fig. 1

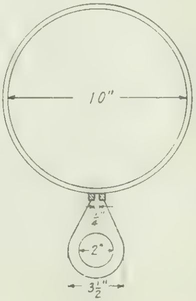


Fig 2

Methods now used for sampling liquids automatically, as far as the writer is aware, all give a sample the volume of which is dependent upon the time element and bears no relation to variations in flow of the liquid sampled. Thus if a drip sample is taken, a small flow through the main pipe line adds just as much to the sample as a large flow. If at the same time the composition of the juice varies, it is evident that such a sample cannot be representative of the total juice flowing.

Fig 3

A sample proportional to the total flow may be obtained by the circular weir shown in Fig. 1. The sample is that portion overflowing through the vertical slot. This device can be applied wherever the liquor to be sampled flows into a receiving tank, measuring tank, defecator, etc.

Instead of the juice or liquor running into the tank through a downward turned nipple or fitting, this is turned up so that the pipe fills and the juice spills over the level edge of the fitting. The size of the sample obtained is dependent approximately on the relation between the width of the slot and the total weir circumference. Actually, the sample will be smaller than indicated by this proportion, on account of the fact that the sides of the slot restrict the flow somewhat. The depth of flow is the same, however, for the slot and for the balance of the circumference.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

A 10-in. in diameter weir with a 0.25-in. slot in a 1-in. wide plate will give a sample of about one one-hundred and twentieth of the total liquid flowing; or with an 0.125-in. slot, one two-hundred and fortieth.

Fig. 2 illustrates the relation between the width of the sample slot and the total weir. A funnel constructed of light sheet metal and soldered to both sides of the slot plate serves to carry off the sample.

If the volume of liquid is very large, it may be necessary to reduce it twice, as in Fig. 3. In a mill grinding 2000 tons of cane per day, the juice may thus be reduced to a bucket sample per 6-hr. shift.

Drainage cocks are indicated to empty the pipe lines at shutdowns. The sampler can be made up of standard pipe fittings in any mill shop.

ADDRESSES AND CONTRIBUTED ARTICLES

Incendiaries in Modern Warfare[1,2,3]

By Arthur B. Ray

Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y.

The destructive action brought about by the natural elements—fire, air, and water—may be looked upon as infinite when compared with the damage which can be caused by other means in a brief period of time. In harnessing one of these natural elements—fire—and applying it as a war weapon, we have assurance of its efficacy in the universal dread in which it is held as the most ruthless enemy of mankind.

The idea of using incendiaries in warfare is not modern; in fact, the use of fire as a destructive weapon dates back to early Biblical times, when burning oils and ignited fire balls consisting of resin and straw were thrown both by the defenders and attackers of fortified towns. In later times crude iron latticework bombs up to 2 ft. in diameter, filled with highly flammable materials, were ignited and projected by catapults or thrown from fortifications. The iron skeleton of such a medieval bomb may be seen in the Tower of London.

But, while, from the earliest times, fire has been considered to be of possible military value, means for scientifically using it as a powerful weapon were not developed until the recent war. The effectiveness of incendiary armament is dependent upon the character of the incendiary materials employed and upon the devices by means of which the materials are carried to the target and set in action there. The development of this type of armament, therefore, involves both chemical and mechanical investigative work which must be done in close coöperation with those who are fully conversant with the military requirements and limitations.

I shall endeavor in this paper to point out the general characteristics of all the typical materials and devices developed by the warring nations and to discuss, in their proper place and in somewhat greater detail, the more important developments with which we were intimately connected in the United States. The materials and devices will be discussed separately in so far as it is possible to do so.

Part I—Incendiary Materials

Since the many devices differ widely as to action, it is obvious that no one incendiary material can be used. In fact, for practically every device a special material has been developed to give the desired result as to time of burning, kind of flame, kind of reaction products, etc. For convenience of discussion, we may classify all the incendiary materials as follows: White phosphorus, thermite, oxidizing agent-combustible mixtures, flammable materials used as such, the special material called "solid oil," and spontaneously flammable liquids.

Phosphorus

On account of its property of igniting spontaneously when exposed to air, white phosphorus was early suggested as an incendiary material, and a number of devices, such as bullets, bombs, shells, and grenades, which depend upon it for incendiary effect, have been developed and used. Against substances which can be ignited by a momentary exposure to a small flame, phosphorus undoubtedly is of value, but for setting fire to materials which are relatively difficult to ignite, phosphorus is of very little value, because of its low temperature of burning and because the phosphoric oxides formed act as an excellent fireproofing material.

Bullets containing phosphorus have proved to be very effective against hydrogen-filled aircraft and against airplanes when the gasoline tank is punctured. The phosphorus pellets which these bullets carry are cast or cut from rods and are coated with aluminium dust—the aluminium acting both as a preservative while handling and as an intensifier of the flame when the bullet functions. The bullets are so designed, as will be shown later, that when fusible plugs in the side are melted by the heat of friction, the phosphorus is exuded and burned. The path of the bullet may be followed by the trail of smoke.

Grenades and 4-inch Stokes' mortar bombs containing phosphorus were effectively used against personnel, particularly when exploded in dug-outs. The inconvenience caused by the obnoxious smoke and scattered burning particles of phosphorus was considerable.

Thermite

The well-known properties of the aluminium-iron oxide mixture called thermite caused it to be widely used, in various modified forms, as an incendiary material. Such mixtures have the advantage that when ignited they produce an enormous amount of heat very quickly and that the molten metal and slag resulting from the reaction will penetrate metal and prolong the incendiary action upon flammable materials. These mixtures when used alone, however, have the disadvantage that the incendiary action against, say, wood structures is confined to a very small area, and that a very large percentage of the heat energy set free is wasted because it is set free too rapidly to be utilized effectively, except by very flammable material. Since

---

[1] Presented before the Division of Industrial Chemists and Chemical Engineers at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] This article is published by permission of the Chief of the Chemical Warfare Service.

[3] Very soon after our entrance into the war the development of incendiary armament was begun in this country by the Bureau of Mines and continued by the Chemical Warfare Service in coöperation with the Ordnance Department. Investigations concerning all the desired forms of armament, except incendiary small arms ammunition which was developed at Frankford Arsenal, were carried out at the American University Experiment Station by the Incendiary Section, under the direction of Capt. Arthur B. Ray, C.W.S., and by the Pyrotechnic Section, under the direction of Major G. A. Richter, C. W. S., with the invaluable assistance of the Ordnance Department.

such material is not often present as the target, the method of placing it with the thermite in the incendiary device was early adopted.

As the primary incendiary material—that which is first ignited and which starts the conflagration—it is believed that thermite is by far the most effective material used. The secondary incendiary material—that which is ignited by the thermite reaction and which continues the conflagration—may be a flammable liquid as such or absorbed in some carrier, or a specially prepared material which will burn for a long time with a large flame and effectively set fire to a difficultly ignitable target. The most satisfactory secondary material is not only capable of burning with a large hot flame, but actually renders the target flammable. Such a material is the solid oil developed by us, which will be discussed later. So, by using thermite in the manner described, the large amount of heat energy suddenly set free is, to a large extent, utilized, and causes the secondary incendiary material to begin its action with a tremendous burst of flame which is most effective.

COMPOSITION—The general military requirements of a thermite mixture are that it be inexpensively prepared in sufficient quantities, that it function properly under all conditions of military use, and that the reaction produce the desired effects. Since it makes no difference what the reaction products are so long as they give the desired incendiary effect, it is obvious that there are possibilities of varying the composition of the mixture greatly. Through the kindness of Mr. Deffler of the Goldschmidt Thermite Co., a number of mixtures in which copper, nickel, manganese, and lead oxides replaced the iron oxides were tested at the company's plant. Also thermite whose constituents were in smaller particles (through 50 mesh) than usual was tested. The results showed that, for our purpose, the incendiary effect of the ordinary thermite was as good or better than could be obtained with the special mixtures.

Manganese dioxide was present in mixtures used by the Germans in certain early incendiary bombs. One particular mixture contained

	Per cent
Manganese dioxide	22.00
Magnetic iron oxide	38.66
Aluminium	16.34
Magnesium	8.45
CaO	1.14
Insolubles	4.24
Resin (by difference)	9.19

The aluminium and magnesium were present in the form of an alloy of the approximate composition Al : Mg = 66 : 34. A mixture of iron oxide, copper oxide, and aluminium was also used.

Thermite mixtures in which were incorporated oxidizing agents other than those necessary for the thermite reaction were investigated but, for our purposes, none were found to possess special merit. It was suggested that sodium nitrate present in large pieces would be melted by the thermite reaction and that the molten nitrate would act as a powerful oxidizing agent and so increase the incendiary action upon the target. After a series of tests, however, it was concluded that the space occupied by the nitrate might better be occupied by thermite. A flaming thermite mixture which contained barium nitrate in addition to the usual constituents was developed and used by the British in their small drop bombs.

It was concluded after many tests that a simple mixture of magnetic iron oxide and aluminium was the most satisfactory, taking all things into consideration, for general military uses. The specifications drawn up for this material state that the mixture shall contain 76 parts by weight of magnetic iron oxides and 24 parts of aluminium. There are, of course, limits to size of particles, purity of materials, presence of foreign substances, moisture, etc.

BINDERS—Since the loose thermite mixture is composed of two substances of quite different densities, it may be rendered nonignitable by vibration, jars, or shocks, because segregation takes place under these conditions. This fact causes it, in the loose form, to be entirely unsuitable for military uses. To obviate this difficulty, the mixture may be compressed or bound into a hard mass by such substances as water glass, sulfur, celluloid, etc.

Preventing segregation by compression is quite possible, as investigations by the British and ourselves have shown. A series of compression tests at various pressures showed that, at a pressure of 12,000 lbs. per sq. in., the density of the ordinary mixture is doubled and the compressed block holds together very well. But, as the density is increased, ignition becomes more difficult, the propagation of the reaction uncertain, and the time of burning longer. In actual tests in drop bombs, the compressed thermite was not considered to give a much better incendiary effect than the same volume of thermite bound together with sodium silicate. The cost of obtaining a given incendiary effect with compressed thermite is, therefore, greater. On account of these facts, the British and ourselves did not recommend compressed thermite for general military use. However, the special flaming thermite which contains barium nitrate is used in the compressed form by the British.

The use of sodium silicate as a binder for the thermite mixture was of course early suggested, since thermite so bound is used in the steel industries. The optimum amount of silicate to use for our purpose was determined by a series of experiments. It was found that the most desirable properties of ignition, propagation of reaction, time of burning, and incendiary action were obtained with thermite bound with 15 per cent by weight of 40° Bé. sodium silicate. The thermite is simply mixed with the sirupy water glass, molded, and baked until dry. The baking operation must be carried out with some care to prevent accidental ignition and to be sure that all the water is driven out. Sodium or potassium silicate was generally used by the other warring nations as a thermite binder. Besides preventing segregation, the silicate binder produces the marked advantage that the blocks react completely, whatever be the position of the point of ignition. The bound material is insensible to shock and shot, which permits its utilization in projectiles of high initial velocity and in offensive devices used by aircraft.

Sulfur seemed to possess certain advantages as a binder, because it combines with the iron formed to give further evolution of heat. Theoretically, a unit weight of a mixture made up according to the equation

$$8Al + 3Fe_3O_4 + 9S = 4Al_2O_3 + 9FeS$$

evolves practically the same amount of heat as the same weight of thermite containing no sulfur but, whereas ordinary thermite contains 24 per cent aluminium, the sulfur mixture contains only 18 per cent. Aluminium is the expensive constituent and this saving of 25 per cent is worth while, provided the mixture has satisfactory properties. But it has one great drawback—when confined it reacts with explosive violence and even when unconfined it burns very rapidly and spatters as small drops, thus lessening the intensive incendiary effect. The pool of molten products from the reaction of ordinary or silicate-bound thermite is most effective in penetrating metal and prolonging incendiary action upon flammable materials. Tests of sulfur-bound thermite did not show it to be as satisfactory for our purposes as the silicate-bound material. It was used, however, by the French in an airplane drop bomb, and its explosive property was utilized to scatter the other ignited incendiary materials contained in the bomb.

Various organic materials such as resin, paraffin, and hard pitch, were investigated as possible binders, without satisfactory results. Celluloid as a binder proved to be fairly satisfactory, particularly where it was desired to get a long flame and uniform burning of the thermite. Thermite bound with 4 per cent celluloid dissolved in a suitable solvent was recommended by us for use in incendiary grenades.

IGNITERS—For the ignition of thermite used in grenades, bombs, and certain projectiles where it is not desired to scatter the reaction products, an igniter, which has no explosive action, must be used. The commercial igniter, which consists of finely divided aluminium and barium peroxide mixed with a certain amount of coarser aluminium and black iron oxide, is satisfactory in this respect, but when loose it deteriorates upon exposure to moisture or when jarred, and then often fails to ignite. It is also readily ignited by passage of a rifle bullet through it. The segregation troubles seemed to be the most serious, however. A large number of mixtures were experimented with in an attempt to find a more suitable igniter, but without entire success. When it is pointed out that an igniter was desired which was stable and not affected by moisture or jarring, which did not react with explosive violence, which was itself ignited by the usual means employed in military practice, which, by its reaction, heated the thermite hot enough (to approximately 1800° C.) to start its reaction, which was not ignited by firing a rifle bullet through it, and which could be inexpensively prepared in sufficient quantities, the failure to develop a perfectly satisfactory igniter is understood. No oxidizing agent which would not react explosively was found better than barium peroxide. Attempts to prevent segregation and moisture attack in the commercial igniter by the use of such binders as shellac and celluloid did not prove successful. So it was concluded that the most satisfactory solution of the igniter problem was to protect the commercial igniter carefully from moisture before using and to prevent segregation by slightly compressing it into a suitable container which was then inserted into a hole in the thermite. This method was used with quite satisfactory results. The igniter can be ignited by a black powder flash, but it is more satisfactory to use a "booster" charge, composed of reduced iron and potassium nitrate pressed on top of it. Such a booster mixture is readily ignited by the flash from a Bickford fuse.

For the ignition of thermite in those projectiles where it is desired to scatter the molten products of the thermite reaction, giving a shrapnel effect, an entirely different sort of igniter must be used. An igniter for this purpose should possess all the safety characteristics of the other type, but should react so rapidly and with such explosive violence as to ignite the thermite and scatter the reaction products. There must be a slight lag between the ignition and explosion, otherwise the unignited thermite will be scattered. The British were successful in developing a satisfactory igniter of this type, called "ophorite," which consists of intimately mixed magnesium powder and potassium perchlorate. Both the British and ourselves attempted to develop a better or a cheaper explosive igniter, without success. Alloys composed of varying percentages of aluminium and magnesium are brittle, and consequently can be readily pulverized. Mixtures of these powders and potassium perchlorate are equal in power to the magnesium mixture, cost less, and have a greater density, but are distinctly more sensitive, and so could not be recommended. Ophorite is much easier to ignite than the commercial igniter and can be readily ignited by a Bickford fuse. Besides its use as a thermite igniter, it was also extensively used as an explosive in gas shell.

Thermite in various modified forms was without question the most generally used and probably the most important incendiary material, but to be most effective it is necessary, as has been pointed out, to use it in conjunction with other flammable materials. Grenades, shell, trench mortar projectiles, and drop bombs containing thermite as one of their essential constituents have been used with marked success.

OXIDIZING AGENT-COMBUSTIBLE MIXTURES

Certain mixtures of what we shall designate the oxidizing agent-combustible type have been used with moderate success in drop bombs and other special devices, but the most important use of such mixtures has been in small arms ammunition and in shell of small caliber where only a very small amount of special materials can be used and where an exact control of the time and character of action is necessary. It is with this type of mixtures that the essential surety of action and nicety of adjustment can best be obtained. Also for use in small unit drop bombs which are intended to ignite readily combustible targets, the advantages of a single mixture which can be relied upon to function properly are evident.

It is quite obvious that devices as different as drop bombs and bullets will require very different types of mixtures for most effective action. The type of mixture desired for drop bombs must, broadly speaking, react to give considerable heat and flame when the bomb lands. There are no exact requirements of weight and no nice adjustment of time of reaction necessary. On the other hand, a mixture which is satisfactory for use in bullets and small shell must fulfil very rigid requirements as to weight per unit volume, time of reaction, character of reaction products and consequent change of weight during the reaction, and finally, character of reaction or incendiary effect. The ballistic requirements are even more important than the incendiary requirements, because the projectiles must be capable of accurate firing to have any effect. The projectiles must have a certain weight and position of center of gravity which must not be greatly changed during flight. By careful arrangement of the metal parts of the projectile or by employing in the mixtures compounds containing elements of high atomic weight, such as lead and barium, the weight requirement can be obtained. By using such a combination of combustible and oxidizing agent as aluminium and lead oxide, for instance, the reaction merely causes a transfer of oxygen, and the volume and weight of the mass are not greatly affected. So the projectile may be capable of incendiary effect during flight and still not be seriously affected ballistically. The duration of the reaction is also very important in those projectiles which act as incendiaries during flight. It should preferably start a short distance from the muzzle of the gun and continue during the effective range of the projectile. The problem of adjustment of time of reaction may be solved by the judicious use of organic substances, which slow down the reaction, or by adjusting the ratio of combustible to oxidizing agent.

The usual oxidizing agents employed in this type of mixtures are the nitrates of potassium and barium, the oxides of barium and lead, and the perchlorate of potassium. Chlorates are used in some cases. The usual combustibles include various finely divided metals, such as aluminium, magnesium, and iron; arsenic and antimony sulfides; sulfur; carbon; and a great variety of organic materials, such as shellac, resin, pitch, paraffin, charred linseed oil, gums, etc. Nitrated organic compounds mixed with combustibles have been used in some devices. Mixtures of inorganic oxidizing agents and heavy oils are effective only when the temperature produced by the combustion of the oil is sufficient to cause the decomposition of the oxidizing agent.

It is, of course, important that these mixtures shall not segregate, and this is prevented either by compression, or by mixing with some substance which acts as a binder, and then heating or compressing. In certain mixtures the magnesium powder is coated with the binding material before mixing with the oxidizing agent. The common binding materials used are sulfur and the organic materials named above. Besides acting to prevent segregation, most of the binding materials cause the mixtures to be less sensitive and the action to be slower. For this reason they are usually spoken of as deterrents. The particular kind of binding material must be chosen with great care because it is a very important component of the mixture.

Very nearly all of the mixtures which have been used with success in small arms ammunition and in small shell for securing tracing and incendiary effects contain magnesium or aluminium —preferably magnesium—for the reason that these metals can be readily oxidized to give an intense heat and brilliant light. The oxidizing agents employed with these metals may be the oxides of barium, lead, or strontium; the nitrates of barium, potassium or strontium; or the perchlorate of potassium. Potassium and barium chlorates have also been used in certain cases.

A mixture of 17 parts barium peroxide and 2 parts of magnesium powder mixed with alcohol and compressed in bullets under a dead weight of around 2500 lbs. has given very satisfactory results. It is ignited very easily by the propellant alone and burns with a very hot, white flame. A mixture of 9 parts red lead and 1 part magnesium or 15 parts red lead and 1 part aluminium compressed into small shell under a pressure of around 15 tons per sq. in. was also used with great success. This mixture must be ignited by a primer, which may consist of 65 parts of potassium nitrate, 13.5 parts of sulfur, 19 parts of powdered antimony, and 2.5 parts of powdered shellac

A typical mixture containing the other type of oxidizing agent consists of 64 parts of barium nitrate, 28 parts of magnesium, and 8 parts of linseed oil. The linseed oil may be boiled or charred, and it acts as a binder and deterrent. Other materials, such as carnauba wax, shellac, and paraffin, have been used for the same purpose. This type of mixture must be ignited by a primer such as the magnesium-red lead mixture previously described. Bullets and some shells containing this mixture have been successfully used.

It should be pointed out that when the mixtures just described are ignited at or near the muzzle and react during flight, the path of the bullet or shell can be traced. Sometimes the tracing effect is of more importance than the incendiary effect. Mixtures which burn with a white light are good tracers at night, but for day tracing a phosphorus filling which emits a smoke trail or a mixture which burns with a red light is preferable. Strontium salts are for this reason used in some mixtures in conjunction with magnesium or aluminium, a deterrent, and sometimes potassium nitrate or barium peroxide. Strontium nitrate, oxalate, peroxide, and carbonate have all been used. A primer is needed to ignite such mixtures. Specific mixtures used in small arms ammunition and shell will be discussed further when the devices themselves are described.

As previously stated, a less important use of the oxidizing agent-combustible type of mixture is in drop bombs and other relatively large devices. Such mixtures were used early in the war, both in larger shell, which were intended to have an incendiary action on impact, and in various drop bombs, but in many cases were later discarded for modified thermite. The Germans made considerable use of this type of mixture, as well as the thermite type, as the primary incendiary material whose chief function was to ignite the other materials in drop bombs. A mixture which may also come under this heading, consisting of 20 parts paraffin and 80 parts of potassium perchlorate, was often used in conjunction with the igniting mixtures.

For use in a small unit drop bomb developed by us which carried only a small amount of material and which was designed to set fire to very flammable targets, a mixture was desired which would give a large hot flame on ignition, burn for several minutes, and leave no protecting residue. A large number of mixtures were prepared and tested as to fitness for this particular purpose. It was found that, of the oxidizing agents available, the chlorates gave best results. Perchlorates were eliminated because, unfortunately, they were not commercially available. The chlorate mixtures burned uniformly with a large flame and with a time factor that could be controlled. Where an oily substance was used as a binder or filler, they passed all the safety tests. Aluminium was found to be the most desirable combustible in conjunction with a binder such as rosin, boiled linseed oil, or asphaltum varnish.

In making comparative tests of the various mixtures a dart filled with the mixture was burned in a standard wooden box open at one end and side only. The effect on the box, the time of burning, the length of the flame, the character of ash, and the weight of material were all taken into consideration in judging the mixture. Such mixtures as looked promising were then put through the surveillance and safety tests. The tendency to segregate, ability to stand a moist atmosphere or a temperature of 140° F. for a week, and sensitivity to sudden shock, to friction, and to vibration were determined. The few mixtures which survived these tests were next tested on a large scale in darts, and the availability of components, cost, safety and ease of manufacture, and the actual incendiary effect were considered. The mixture finally recommended consisted of 54 parts barium chlorate, 16 parts rosin, 14 parts aluminium, and 16 parts asphaltum varnish.

The primer recommended for use in igniting this mixture consisted of reduced iron and potassium permanganate, bound with paraffin. This primer was found to be the most satisfactory, after a large number of tests, as to action and deterioration.

One of the mixtures tested during this investigation and found unsatisfactory consisted of 1 part hexamethylenetetramine and 2 parts sodium peroxide. This mixture attracted considerable attention because of the fact that a Dr. Scheele, taken into custody by the Department of Justice, claimed that it had been used in attempting the destruction of the cargoes of thirty-five vessels. Our experiments with this mixture showed that it has no great affinity for moisture, can be handled without risk in any sort of metal container, and that when ignited by means of sulfuric acid or flash from a Bickford fuse it reacts very rapidly in the open with great evolution of heat and a large flame, but that if confined it reacts explosively. A lead container is ideal for the mixture. The addition of a small amount of heavy oil or talc caused the mixture to burn longer, and reduced the sensitiveness. The British also experimented with this sort of mixture and found that sodium benzenesulfonate could be successfully used in place of the hexamethylenetetramine. For use in certain small drop bombs a modified form of this peculiar mixture has possibilities. After many large-scale tests it was concluded that it is not a satisfactory material for use in the larger incendiary devices. Dr. Scheele's extraordinary claims for the mixture were never substantiated.

Flammable Materials Used as Such

The flammable materials used as such without any particular treatment or admixture of oxidizing agents, etc., include phosphorus (previously discussed), resins, pitch, sodium, celluloid, and the various sorts of flammable liquids and oils. Certain of these substances were used as the secondary incendiary material in projectiles and drop bombs, but the most important are the oils and liquids used in flame projectors.

Almost any liquid which will burn will, of course, have some incendiary effect, but a liquid which will satisfy all the military requirements and give the maximum incendiary effect in any particular device can be developed only by a critical study of both physical and chemical properties, and after many tests. While the actual heat of combustion of a liquid is a determining factor, it is not the deciding factor in causing it to be rejected or accepted for incendiary purposes. The fact that it vaporizes too readily, has a fire point which is too high, or leaves a fire-proofing residue on burning may cause a liquid with an exceptionally high heat of combustion to be rejected. The manner in which it is to be used or ignited determines the desired properties. A liquid which must be ignited by an explosion of black powder, as in certain types of drop bombs and projectiles, or by momentarily coming in contact with a small flame, as in flame projectors, must contain a definite minimum percentage of a constituent with a very low fire point, such as carbon disulfide, gasoline, or benzene; but a liquid which has a relatively high fire point may be satisfactorily used in conjunction with primary incendiary materials which react with a large evolution of heat.

The chief requirements of a liquid mixture for use in flame projectors are that it must be readily and easily ignited, must not have too low a specific gravity, since a light mixture tends to spray at the nozzle of the projector and so decrease the range, and must be of such a character that combustion does not occur needlessly during the passage of the stream through the air or, to any large extent, until the stream has reached its objective. In other words, the desired object is attained when the ignited *liquid* is thrown upon the target some distance away. It is not desired merely to project a flame.

With these considerations in mind, an extended investigation of liquid mixtures for use in the American flame projectors was carried out. Mixtures of various liquids, such as gasoline, kerosene, carbon disulfide, turpentine, benzene, water-gas tar, petroleum distillate, fuel oils, gas oils, and others, were tried out. It was early found that the heavier mixtures, provided they are not too viscous or too volatile, give a better trajectory, that is, tend to spray less and are thrown farther than the light mixtures. The heavy liquids also burn farther away from the nozzle, which is very desirable for the operator's comfort, are more resistant to wind pressure, and carry sufficient unburned material to saturate and render the target highly flammable. The most satisfactory mixture, therefore, consists of a heavy, rather viscous oil or tar and a more fluid and more flammable liquid. For the heavy viscous liquid, water-gas tar (sp. gr. 1.044 and flash point 122°) was found to be most satisfactory from all standpoints. Mexican fuel oil was also found to be very good. For the light flammable liquid, benzene heads (sp. gr. 0.756 and flash point 26° C.) or crude benzene were used with most success. To determine the most desirable proportions, a series of mixtures, containing from 50 to 90 per cent of the heavy constituent, were tested. It was found that a reduction of the volatile constituent below 30 per cent caused poor ignition, and that any great increase caused the trajectory to be poor, and produced a rolling type of flame which did not leave any unburned liquid at the end of the stream.

A mixture of specific gravity 1.02, containing 70 per cent water-gas tar and 30 per cent benzene heads, was first recommended. It gave an excellent trajectory, fierce flame, and good throw. Crude benzene was later substituted for the benzene heads, as being more readily available in the desired quantities Forty per cent crude benzene gives best results, but in hot weather it can be reduced to 30 per cent. Approximately 30 per cent of this oil mixture is unburned at the end of the trajectory, and in jet shooting as small a quantity of liquid as 0.5 gal. can be thrown the full distance of approximately 100 ft.

Combinations of heavy and light liquids were used by the other warring nations, the actual liquids used being those most readily available. The British, French, and Italians used mixtures of heavy and light petroleum distillates with a specific gravity of about 0.86 at 15° C. The Germans used various mixtures of heavy petroleum distillates or heavy wood-tar and coal-tar fractions with light petroleum distillates, coal-tar fractions or, sometimes, such liquids as methanol, acetone, and even ether. The specific gravity of the mixtures was usually about 0.96 at 15° C.

The ignition of projected liquids was effected by us by means of a hydrogen pilot lamp at the nozzle. Considerable experimentation with various other types of igniters was carried out, but the hydrogen pilot flame was considered best. It has the advantages, of course, of being nonluminous when the machine is not in action and giving positive ignition when needed.

Many methods of ignition were used by other nations. A cartridge of a slow burning, oxidizing agent-combustible mixture attached to the nozzle and ignited by an electric detonator or by friction was successfully used. In some cases incendiary hand grenades were thrown out to ignite the projected flammable liquid.

When used in bombs and projectiles the flammable liquids may be absorbed in some such material as cotton or jute waste to prevent too rapid volatilization and burning. Such an arrangement possesses the disadvantage that if the mass is scattered by an explosion the intensive incendiary action is lost, and if it is allowed to burn without scattering, the mass of absorbent material protects the target to a considerable extent. Liquids and mixtures of paraffin and light oils which are somewhat mushy have objectionable hydrostatic effects when used in drop bombs and projectiles.

Besides the flammable liquids, various other organic materials, such as resins and pitches, have been used. Celluloid was used in several German incendiary devices and, mixed with resin, in a French bomb.

SOLID OIL

The special incendiary material known as "solid oil" was developed as a result of an extended investigation of materials which could be used most effectively along with thermite in devices such as our 50-lb. drop bomb, which were designed to set fire to heavy building constructions. It was early decided that such devices should contain some quick-reacting, great heat-producing material, such as thermite, and a greater amount of flammable material which, when ignited by the thermite reaction, would burn with a large hot flame for a considerable time, and actually render the target more readily flammable. Aside from these desirable properties, the material should present no great problems of manufacture, cost, transportation, or use.

In early tests various oxidizing agent-combustible mixtures, pine pitches and rosins, heavy oils alone, and absorbent materials saturated with oils were tried, but all were found to possess undesirable properties. After comparative tests it was clearly seen, however, that the oils possessed the most desirable incendiary properties and that the only drawback to their use was their physical state. Experiments were accordingly started to determine the feasibility of solidifying satisfactory oil mixtures. It was well known, of course, that emulsions or gels could be prepared by the use of a number of colloidal substances. After considerable investigation a process was developed whereby we could prepare simply and cheaply a solidified oil mixture which has stood all the tests of permanence under conditions of transportation and use, and which has proved to be as near the ideal secondary incendiary material as could be desired. The mixture is run into the containers while still warm and fluid, and becomes solid on cooling. After the process had been in use for some time, Dr. H. G. Byers made a survey of the American, French, British, and German patents relative to solidifying fuel oils and, from the five hundred found, he selected forty-five as being most representative, and tested them in the laboratory. The products obtained were compared with the standard solid oil. He states that "none of the products were found to compare very favorably with it. * * * Those that were found to approximate the standard oil now in use were much more complex and probably more expensive."

The flammable liquids used in the preparation of the material were selected after tests of over two hundred oils and mixtures had been made. A large number of highly flammable liquids burn at a fairly low temperature, and such liquids will not effectively ignite the wood upon which they burn or render it highly flammable. Solidified alcohol is an example of such a material. Materials that vaporize very rapidly keep the wood cooled down below its ignition temperature. Furthermore, such materials burn so readily that they do not melt and spread so as to increase the area of attack. Solidified light oils and liquids with a low fire point are not satisfactory. On the other hand, solidified heavy oils and greases with a very high fire point are not satisfactory because they melt and burn too slowly, because the liquefied portion which runs away from the point of attack does not remain ignited, and because, in some cases, a residue which protects the wood is left upon burning. Our experiments showed that a solidified mixture containing a small percentage of a liquid having a relatively low fire point and a large percentage of a liquid having a moderately high fire point was most effective. Such a mixture burns readily, owing to the presence of the liquid of low fire point, and the burning of this liquid furnishes the heat necessary to melt the material and keep ignited the liquid of higher fire point which spreads over a large area, penetrates the wood, and actually renders it highly flammable. Certain readily available distillate fuel oils with a range of fire points from 170° to 225° C. were found to give most satisfactory results. Distillation curves and fire-point determinations were of great value in the search for suitable liquids.

The preparation of the solid oil on a large scale for filling the 50-lb. drop bombs presented no difficulties, and a plant for the work was put into operation at Edgewood Arsenal.

Besides its use in these large bombs, solid oil was also used or recommended for use in other devices such as Liven's drums, shell, grenades, certain other types of bombs, and in trench stoves. For this latter use a special stove was designed which permitted the oil to burn without smoke. Solidified kerosene was found to burn satisfactorily in these special burners. In tests, 100 g. burned continuously with a luminous, nonsmoky flame for 6 hrs. In respect to heating power this material is greatly superior to the well-known solid alcohol.

Spontaneously Flammable Liquids

For the reason that it would require no ignition device and thus could be advantageously used, a liquid was desired which would ignite spontaneously after a short exposure to the atmosphere, have an effective incendiary action, and be safe to handle and transport. Simple, spontaneously flammable liquids such as zinc ethyl and carbon disulfide containing dissolved phosphorus obviously could not satisfy the requirements, and considerable research was necessary before a satisfactory liquid was produced. In the course of the research the possibilities of using such substances as phosphine, silicine, chromyl chloride, fuming nitric acid, permanganates, zinc ethyl, and phosphorus were fully investigated, and the substance found most suitable for the preparation of such liquids was phosphorus.

A number of combinations of liquids were developed which gave satisfactory results as far as spontaneity of ignition was concerned. But what was desired was a homogeneous liquid with the desired properties. Mixtures were made of various oils with carbon disulfide and phosphorus containing these constituents in such proportions that the separation of no solid or liquid layer resulted. The objection to these mixtures was that they lacked intensity of combustion, so the effect of adding various nitrated organic compounds was tried. Of the nitro bodies, trinitrotoluene was found most satisfactory. Finally, a mixture containing crude benzene, steam-distilled fuel oil, gas-tar oil, carbon disulfide, phosphorus, and trinitrotoluene was developed which is satisfactory from the standpoints of simplicity of preparation, safety, and effectiveness. By varying the proportions of the constituents the ignition can be made to occur either almost instantly upon exposure or after a considerable delay.

In the preparation of the mixture the desired quantity of trinitrotoluene is dissolved in the corresponding weight of benzene, the fuel oil and gas-tar oil are added, and the whole is stirred until homogeneous. The solution of phosphorus in carbon disulfide, prepared by introducing the phosphorus beneath the surface of the disulfide with as little exposure to air as possible, is added to the previously prepared oil mixture, and the container is closed and agitated to insure homogeneity. With proper precautions, the handling of the solution can be done without danger of premature ignition.

The speed and spread of ignition are secured by the presence of the readily volatile constituents and the duration and intensity of the flame by the presence of the heavier combustibles. The mixture is not subject to detonation by shock and, having a low coefficient of expansion (0.0174 per ° C. between —10° and 55°) and a low vapor pressure (58 cm. at 50° C.), will not cause undue pressure in the containing device. It may be used alone or with an absorbent such as cotton waste in any sort of a device designed to carry liquid or semiliquid material. The 8-in. Liven's projectiles containing the mixture and cotton waste were quite effective in trials.

(To be concluded)

Assignment of Patents

On June 2, 1921, a decision was given by the Supreme Court of the State of New York in the case of the Air Reduction Company, Inc., against Warren R. Walker, a research chemist who refused to assign a patent to the company. The company is engaged in the manufacture and sale of oxygen, acetylene, calcium carbide, and oxyacetylene welding and cutting apparatus and in the development of processes and apparatus for the utilization of the elements of the atmosphere, and maintains a research laboratory for the study of the utilization of nitrogen, argon, neon, and other by-products of the manufacture of oxygen, under the direction of Floyd J. Metzger, chief chemist. The defendant was employed as a research chemist, and in March 1920 was engaged in an investigation on the commercial utilization of neon under the direction of Metzger, devoting full time to this problem at the sole expense of the company and fully understanding that the condition of his employment was the assignment to the company of all inventions made during his employment. In June 1920, an automobile indicator was devised which embodied a neon tube bent in the outline of a hand and mounted in a casing with an induction coil, adapted for mounting on an automobile or other motor driven vehicle. This invention was patented by the company in the joint names of Floyd J. Metzger and Warren R. Walker. As a result of further investigations, while still in the employ of the company, Walker materially improved the invention. Throughout the period of his employment the defendant never indicated an intention to claim any interest whatsoever in the invention, and, together with Metzger, executed the papers in connection with the filing of the application for the patent by the company. When requested to execute an assignment of the application in order that the legal title might rest in the name of the company, he refused to do so, although Metzger assigned his half of the invention. The invention is of great value to the company, and the holding by the defendant of the legal title to a one-half interest in the invention, the equitable title to which is in the plaintiff, might lead to the substantial damage of the company for which no adequate remedy at law exists. In view of the above findings of fact, the Court ruled that the plaintiff is the lawful owner of the entire right, title and interest in and to the application for this patent in this and any foreign company, and that the defendant should assign it to the plaintiff and deliver to plaintiff all documents and models relating to the invention or any improvements made by him while in the employ of the plaintiff; that the defendant must give the plaintiff all information regarding patents on inventions made during his employment by the company; that the defendant is permanently enjoined from making or selling any automobile indicators embodying a tube containing neon as illustrated in above patent or improvements, from assigning to anyone except the plaintiff his rights in such patents, from filing any additional application for patents on automobile indicators or any other inventions made while in the employ of the plaintiff, and from attempting to interfere with the prosecution of the application for the patent on this invention.

Industrial Alcohol and Its Relation to Prohibition Enforcement from the Manufacturer's Standpoint[1]

By **M. C. Whitaker**

U. S. Industrial Alcohol Co., 27 William St., New York, N. Y.

The Chemical Profession has cause to be concerned over the present and future status of alcohol for legitimate industrial and scientific purposes. They may well ask such questions as: Why am I unable to get alcohol to continue the manufacture of U. S. P. medicinals, antiseptics, flavoring extracts, perfumes, and the infinite variety of daily household necessities requiring pure alcohol in their production? Why is it so difficult for me to get alcohol for scientific use for research and for educational purposes? Why do I have to pay a tax of 1000 per cent on alcohol used in my industry, when we have a fifteen-year-old law giving us tax-free alcohol for industrial purposes? What has the prohibition of intoxicating liquors got to do with alcohol for industrial uses and for purposes of national defense?

Let us first clarify our problems, and then possibly suggest remedial measures.

THE CONTRADICTORY PROVISIONS OF THE VOLSTEAD ACT

The National Prohibition (Volstead) Act, "To prohibit intoxicating beverages, and to regulate the manufacture, production, use, and sale of high-proof spirits for other than beverage purposes, and to insure an ample supply of alcohol and promote its use in scientific research and in the development of fuel, dye, and other lawful industries," was passed with three principal divisions, or Titles:

> Title I—To provide for the Enforcement of War Prohibition (automatically replaced by the second section (Title II) which became operative on January 16, 1920, the effective date of the XVIII Amendment).
>
> Title II—Prohibition of Intoxicating Beverages.
>
> Title III—Industrial Alcohol.

Alcohol is defined in the prohibition section of the Volstead Act as follows:

> The word "liquor," or the phrase "intoxicating liquor," shall be construed to include alcohol, brandy, whiskey, rum, gin, beer, ale, porter and wine, and in addition thereto any spirituous, vinous, malt or fermented liquors, liquids and compounds, whether medicated, proprietary, patented or not, and by whatever name called, containing one-half of 1 per cent or more of alcohol by volume, and which are fit for use for beverage purposes.

The same alcohol is defined in the Industrial Alcohol Section of the same Act as:

> The term alcohol means that substance known as ethyl alcohol, hydrated oxide of ethyl, spirit of wine, from whatever source or whatever process produced.

Thus it is, at the very outset of our problem, that law has combined with nature to give a Dr. Jekyll and a Mr. Hyde character to one of our greatest chemicals, alcohol.

Under the prohibition section of the law, it is unlawful to advertise, manufacture, sell or possess for sale, any utensil, contrivance, machine, preparation, compound, tablet, substance, formula, direction or recipe, advertised, designed or intended for use in the manufacture of alcohol, or it is unlawful to solicit or receive, or knowingly permit an employee to solicit or receive from any person an order for alcohol, or give any information as to how alcohol may be obtained, subject to certain specific exemptions.

It is provided on the other hand in the Industrial Alcohol Section of the law, Section 13:

> That the Commissioner shall from time to time issue regulations respecting the establishment, bonding, and operation of industrial alcohol plants, denaturing plants, and bonded warehouses authorized herein, and the distribution, sale, export, and use of alcohol which may be necessary, advisable, or proper, to secure the revenue, to prevent diversion of the alcohol to illegal uses, and to place the nonbeverage alcohol industry and other industries using such alcohol as a chemical raw material or for other lawful purpose upon the highest possible plane of scientific and commercial efficiency consistent with the interests of the Government, and which shall insure an ample supply of such alcohol and promote its use in scientific research and the development of fuels, dyes, and other lawful products. All regulations so issued shall have the force and effect of law.

Under one section of the law you are forbidden to whisper the terrible word, because of its booze associations, while under the other section you are required to proclaim alcohol from the housetops as a national necessity.

In the administration of this law, when there is an apparent conflict of language, the prohibition officers appear to work under the injunction usually given to beginners learning to drive an automobile: "When in doubt, push both feet." Prohibition is regarded by them as their first duty, and when in doubt, "stop everything—engine and all."

EXAMPLES OF INTERPRETATIONS OF THE VOLSTEAD ACT

Narrow rulings under these provisions have led to such ridiculous interpretations as may be illustrated by the following instances:

(1) The General Counsels of the Telephone Company in both Boston and Baltimore advised their clients that the listing of the name "U. S. Industrial Alcohol Co." in the directory would be an illegal act under the prohibition law. The Company was obliged to obtain an official ruling from Washington in order that its corporate title might be listed in telephone books.

(2) The Prohibition Commissioner, under date of March 22, 1921, advised the U. S. Industrial Alcohol Company that the use of the words "Cologne Spirits and Alcohol, Pure and Denatured" on their letter heads (standardized for fifteen years) was illegal under the prohibition act, and must be stopped. As result of an appeal to the solicitor of the Internal Revenue Department, this ruling was finally reversed under date of May 12.

(3) E. B. Badger & Sons, of Boston, attempted to purchase a copy of "Young's Fractional Distillation" from a local book store, and were advised by clerk that they had the book, but that it could not be sold under the prohibition law. On May 6, 1921, the following letter, signed by John F. Kramer, Prohibition Commissioner, was directed to Badger:

> Gentlemen: Replying to your letter of April 29, 1921, you are informed that if Young's "Fractional Distillation" is a scientific publication which is commonly used by scientists, this office perceives no reason why it should not be purchased by you for the use of your engineering department.
>
> This office issues no permits to enable scientific persons to procure such technical works, but it is anticipated that this letter exhibited to any book seller who has such a work for sale will serve the purpose.

(4) On May 15, 1920, the U. S. Industrial Chemical Company of Baltimore delivered to the steamship piers 32 drums of isobutyl alcohol for export to France. The ship's agents refused to accept the goods, because he noted the word "alcohol" on the packages and in the bill-of-lading, stating that they were not permitted under the prohibition laws to handle alcohol.

The goods had to be reloaded, trucked back to the plant, a round trip distance of twelve miles, relabeled and new bills-of-lading prepared under the name "Iso Butyl Solvent." Under this name the steamship company accepted the consignment, and the reason for the disguise had to be explained to the French buyers as well as such a thing can be explained to a chemist of a sister Republic.

(5) The Bishop Gutta Percha Company applied for a permit to use tax-free alcohol in their laboratories. The answer to the application, under date of May 6, contains the following paragraphs:

> This permit is granted on condition that the permittee agrees to keep on hand a stock of tax-paid alcohol for the routine work of the laboratory and that the tax-free alcohol withdrawn under this permit will be used only for original research and development work. When the research work has been

---

[1] Presented before the New York Section of the American Chemical Society, New York City, June 10, 1921.

developed into an actual working process and the function of the laboratory is merely to continue the operation of this process, tax-free alcohol may not be used.

Routine work such as tests or analyses for purity of various materials both during the process of manufacture and in determining the purity of the finished product does not appear to be exclusively scientific research, and tax-paid alcohol should be used for such purpose.

THE RELATION OF PROHIBITION REGULATION TO INDUSTRY

Chemists as a profession are not concerned with prohibition, except possibly to consider it and classify it in its proper place in relation to industrial economics and national defense.

Prohibition cannot be classed as a national necessity, and it certainly is not even a luxury; it is a great social experiment which the United States has determined to try. Such a social experiment need not and should not be so administered as to interfere with the economic needs or the national defense requirements of the country, any more than a similar experiment should be permitted to disorganize the working forces, or interrupt the production of your factory.

The spotlights of the world are turned on the prohibition administration of the United States; little wonder they are nervous and jumpy. Even under this strain they must not be permitted to disregard the fundamental principles of business economics and national welfare, in order to carry through an ambitious experiment in sociology.

Mr. Wayne B. Wheeler, General Counsel of the Anti-Saloon League, made, before the Judiciary Committee, on Friday, May 20, 1921, the following very significant statement: "If it comes to the point where it must be a choice between medicaments for medical preparations and the enforcement of the law, I think we must choose law enforcement."

Mr. C. R. O'Connor, until recently Federal Prohibition Director of New York, is reported to have said, in answer to a protest by manufacturers in regard to the reluctance of his office to approve permits to secure alcohol for their industrial operations, "Industrial Alcohol be damned; you know it's all booze!"

One of the greatest difficulties connected with the separation of industrial alcohol from prohibition enforcement is reflected in these two statements by high authorities in the Prohibition Enforcement program. The do-or-die fanaticism reflected in Mr. Wheeler's statement, and the utter lack of knowledge as to the existence of an industrial alcohol problem, as reflected in Mr. O'Connor's statement, represent the frame of mind of ninety per cent of the prohibition advocates.

It is a notorious fact that the Anti-Saloon League dominates prohibition legislation and enforcement. When the prohibition law to enforce the Eighteenth Amendment was presented to the Judiciary Committee by Mr. Wheeler, it consisted of what are now Titles I and II, for the enforcement of prohibition, with absolutely no provision for industrial alcohol. What is now Title III, the Industrial Alcohol Section of the prohibition bill, was drafted and introduced as a government measure at the direct suggestion of the then Commissioner, Daniel C. Roper, in order to save industrial alcohol. It was through the foresight and influence of the officials of the Bureau of Internal Revenue, and not due to any consideration on the part of the promoters of the Anti-Saloon League Bill, that the bills presented to Congress to enforce prohibition carried any provision whatever for industrial alcohol.

NEED OF EDUCATION OF PUBLIC AS TO INDUSTRIAL ALCOHOL

The entire disregard of the right of existence of alcohol, the chemical, for industrial purposes can be explained only on the assumption that they are totally lacking in knowledge of its essential relations to chemical industry and to national defense, and that they do not understand its relation to their home comforts, to the health of themselves and their families, and to the progress of science. Granting this ignorance, it is not surprising that they believe and advocate, as the best method of enforcing prohibition, the complete extermination of all alcohol.

This is a condition for which the chemists, in a large measure, are responsible, and a condition which they and the industries using alcohol can and must remedy. They have not adequately educated the public, who make and enforce our laws, in the matter of the essential needs of chemical industry. To educate that public is a big contract, but it must be undertaken and successfully carried through by the chemists working individually and collectively, if alcohol, and all industry directly and indirectly related to it, is to be saved.

Chemists look upon alcohol as one of the most essential and important materials of their industry. They put it in the same class with sulfuric acid, benzene, or caustic soda. They know there can be no great development of chemical industry without alcohol, any more than there could be a steel industry without pig iron, an electric industry without copper, or a fertilizer industry without potash and fixed nitrogen. While alcohol may not be used directly in the manufacture of textiles, automobiles, or sugar, any chemist can draw a flow sheet to show its relation to some of the contributing industries.

Furthermore, petroleum experts issued a warning at the last meeting of the AMERICAN CHEMICAL SOCIETY in Rochester, in regard to the visible supply of liquid fuels, which ranks in importance with the famous warning of Sir William Crookes in reference to nitrogen for fertilizer. They pointed out that, in from fifteen to twenty years, the rapidly diminishing supply of petroleum will compel the world to turn to some other source for liquid fuel. The only possible solution to the problem in this distressingly short time is alcohol.

TAXATION OF INDUSTRIAL ALCOHOL

Taxation of alcohol has grown out of the habit of taxing alcoholic beverages. There is no more reason why a tax should be levied against alcohol (the chemical) than there is for levying a tax against sulfuric acid, caustic soda, benzene, or coke. Congress voted in 1906 tax-free alcohol for industrial and scientific purposes, and properly retained at that time the tax on beverage alcohol. This action of Congress was reiterated in the industrial alcohol law of 1913, and again in Title III of the prohibition act of 1919. The sub-title of the 1919 act and Section 13 of the same act have already been quoted in this paper.

In view of the above declared purposes of Congress in the alcohol acts of 1906 and 1913, and in the title and body of the prohibition act, what justification can there be for imposing a tax upon alcohol used in medicinal, proprietary, toilet, antiseptic, and flavoring extract industries?

The Government has already gone far beyond the advice of its own legal experts and the intent and purpose of Congress in exacting a tax of 1000 per cent upon the alcohol used in these industries. This is an indirect tax upon the users of the products of these industries; that is to say, the unfortunate sick who have to use U. S. P. and proprietary medicines, the fastidious who use toilet and antiseptic preparations, and the housewives who use flavoring extracts and sirups; and in spite of all this legislation on behalf of industry, may they still rule that the analytical and works control chemist must pay a tax of 1000 per cent upon the alcohol used in his routine work?

ADMINISTRATION OF THE PROHIBITION ACT

The Industrial Alcohol Section of the National Prohibition Act (Title III) theoretically became effective on October 28, 1919, although administrative regulations (No. 61) were not approved thereunder until January 31, 1920, and February 5, 1920.

Laws will not administer themselves, and this is especially true of the National Prohibition Act. No provision whatever was made by the Government, at the outset, to separate the administration of industrial alcohol from prohibition. Under the ceaseless pressure of the Anti-Saloon League, all energies were arbitrarily directed to organizing for, and administering, prohibition, while the industrial alcohol provisions of the law were literally lost in the fog.

The situation for alcohol for the industries, for research, and for education became so serious that, in June 1920, a large committee, representing leading educators, investigators, chemical societies, consumers and producers, and the War and Navy Departments, journeyed to Washington, and strongly protested at the neglect of the legitimate alcohol industry in the scramble to enforce prohibition.

This protest finally resulted, in October 1920, in the creation of the Division of Industrial Alcohol and Chemistry, under Captain D. S. Bliss, Deputy Prohibition Commissioner, with Dr. J. M. Doran, of the Bureau of Internal Revenue, a chemist of high professional standing and long experience, in charge.

When a government department assumes control of an industry, it assumes an obligation to the nation as a whole, which I am sorry to say is not always recognized, and that is an obligation to govern well and govern wisely. Ignorance of the industrial needs and economic requirements is no excuse for "pushing with both feet when in doubt" and no excuse for "stalling the engine."

This Division has not had an opportunity to achieve the full measure of its importance because it is still subordinated to the prohibition provisions of the law. A Division of Industrial Alcohol and Chemistry, directed by competent chemists equipped with adequate facilities, and charged with the full responsibility of administering all alcohol for industrial, scientific, and nonbeverage uses, is clearly implied when industrial alcohol is given a separate section of the law, and the legal provisions to "*place the nonbeverage alcohol industry and other industries using such alcohol as a chemical raw material or for other lawful purpose upon the highest possible plane of scientific and commercial efficiency*" are made mandatory.

The chemical profession and the chemical industry should unite to make the Division of Industrial Alcohol and Chemistry what it is legally stated to be, and what the economic future of this country demands that it should be—an organization to control alcohol, the chemical.

THE NEW BILL, H. R. 6752

Let us turn our attention to the new bill now before the House, which is a further encroachment upon chemical industry. The development of industry as a whole is a matter of bread and butter to the chemist; the greater that development, the more bread and the more butter will be available to those men who have chosen chemistry or the chemical industry as their profession. New legislation, of which we are threatened with a surfeit, and which threatens chemical industry, deserves the attention of all chemists.

This new bill (H. R. 6752) introduced by Mr. A. J. Volstead, *chairman*, Committee on Judiciary, and sponsored by Mr. Wayne B. Wheeler, counsel of the Anti-Saloon League, is admittedly intended to prohibit beer, although the word "beer" is not used in the proposed act.

You have all heard of "jokers" in legislative enactments. This bill is a "fleet of jokers," some of which are extremely important to those of us who are dependent for our living upon chemical industry.

The first sentence in Section 2, prohibiting beer without saying so, is characteristic of the subtle and evasive character of the wording of other provisions of the bill. Stripped of legal verbiage, the bill provides:

1—For the prohibition of beer, without using the word "beer."

2—The granting of arbitrary power to the Commissioner of Internal Revenue to substitute his lay judgment for that of the professional physician in the matter of the kind and amount of wines that may be prescribed in case of sickness.

3—For the arbitrary limitation of the prescribing or selling of wines containing more than 24 per cent alcohol and more than one quart to any one person in ten days.

4—For limiting the number of prescriptions a physician may write to one hundred in ninety days.

5—For limiting, by the Commissioner of Internal Revenue, the amount of spirituous liquor which may be imported into the United States.

6—For limiting, by the Commissioner of Internal Revenue, the amount of liquor for medicinal purposes, save alcohol, to be made in the United States.

7—For the cancellation of permits to manufacture (*a*) U. S. P. or N. F. medicines, (*b*) proprietary medicines, (*c*) toilet, medicinal, and antiseptic articles, (*d*) flavoring extracts, if he shall find that they are "*being purchased* for use as a beverage, or for intoxicating beverage purposes."

8—For the replacement of all alcohol-bearing substances (*i. e.*, whisky, brandy, wines, etc.) in U. S. P. medicines, proprietary medicines, toilet, medicinal and antiseptic articles, flavoring extracts and sirups, by alcohol.

9—For the securement of a permit to manufacture products (which under existing law must be unfit for beverage purposes) such as U. S. P. medicinal preparations, proprietary medicines, toilet, medicinal and antiseptic preparations, flavoring extracts, sirups, etc., in which alcohol is used.

10—For the serving of notice of such an application on the Attorney General.

11—For the public posting of notice of intention to manufacture such articles at the place of business of the manufacturer.

12—That any federal or state officer, or any person authorized by such officer, may oppose the application.

13—For the arbitrary power for the Commissioner to revoke permits to manufacture.

14—For the Attorney General to designate some suitable person or persons to perform the duties imposed upon him by this Act.

15—For the extension of the provisions of this supplemental Act to the territories, including Hawaii, and the Virgin Islands.

16—For conferring jurisdiction upon the Courts in the territory of Hawaii and the Virgin Islands to enforce the National Prohibition Act.

17—For regulations to carry into effect the provisions of this Act.

18—For fines and, or, imprisonment as provided in the National Prohibition Act, as follows:

> Any person who manufactures or sells liquor in violation of this Title shall for the first offense be fined not more than $1,000.00 or imprisonment not exceeding six months, and for the second or subsequent offense shall be fined not less than $200.00 nor more than $2,000.00 and be imprisoned not less than one month or more than five years.

For purposes of discussion, the bill may be divided into three parts:

1—The prohibition of beer, and limiting prescriptions.

2—The extension of governmental control, under the guise of prohibition, to the U. S. P. medicines, the proprietary, the perfume, and the flavoring extract industries.

3—The penalties.

Again we as a profession are not concerned with the prohibition features of this bill. It might be fair to assume that our professional associates, the medical men, would wince at the idea of having the judgment of a Commissioner of Prohibition supersede that of the 150,000 medical practitioners in the United States.

Government control of industry is not a new idea. The railroads, the telegraphs, and many of our industries will have reason for many years to appreciate the full meaning of government control brought about by the war. The past administration deserves to go down in history's Hall of Fame for having demonstrated the complete impracticability of government control of industry.

Nevertheless great ingenuity will continue to be displayed by those with socialistic tendencies, in the invention of subtle means to effect government domination of industrial activities. We shall have such schemes as control by means of government administered patents, control of industries affecting the farmer, control through tax interest in products and profits under the guise of taxation for revenue, and finally control as a means of administering social reform.

The proposal to include under this bill a group of industries, conforming in every respect to the provisions of the Eighteenth Amendment, the National Prohibition Act, and every other law of the land, is plainly an effort to extend government control where it is neither necessary nor desirable.

Your home town laws used to require a man who proposed to open a saloon in a neighborhood to post a notice of his intention upon the doors and walls of the building, in order that the whole neighborhood might be advised of the impending stigma that was about to be placed upon it, and have an opportunity to work up opposition.

Similarly, the pending bill in the case of a manufacturer proposing to engage in the business of making pharmaceutical, proprietary, toilet and antiseptic articles, or flavoring extracts, requires that "Notice thereof shall be served on the Attorney General and *publicly posted* at applicant's place of business * * * * " and further, "any Federal or State Officer or any person authorized thereto by any such officer may oppose any such application." Why should a legitimate chemical industry and its owners and employees be stigmatized and put in the class with the corner saloon or the bootlegger, and the clear implication held out that he is engaged, or is about to engage in a business of questionable character? Why should legitimate business plans be disclosed by "notice of intention," and why should another opportunity be created, by law, for graft?

Another provision of the bill gives concurrent power to the Commissioner of Internal Revenue and to the Attorney General, and also provides that the Attorney General may designate "some suitable person or persons to have charge of and perform the duties imposed upon him by this Act."

This means, in plain English, that these legitimate industries, because they require and use alcohol, will have to submit their business, their operations, and their employees to control, not only by two independent government departments, but also by an additional unknown quantity designated as "some suitable person or persons." Who do you think it or they will be? The risks of doing business under such conditions would alienate legitimate investors.

No chemist could afford to risk a fine of $1000 or a jail sentence for five years for some alleged or technical violation of the law. Such provisions as these stigmatize an important division of chemical industry, and that stigma passes to the chemical profession as a whole. Successful enforcement of prohibition requires the coöperation of the chemists to a greater extent than that of any other profession, and that coöperation cannot be obtained by wholly unnecessary or misdirected stigmatization.

Does the spirit of the proposed bill conform to the principle of placing "the nonbeverage alcohol industry and other industries using such alcohol as a chemical raw material, or for other lawful purposes, upon the highest possible plane of scientific and commercial efficiency," as already provided in the Industrial Alcohol Section of the existing Prohibition Enforcement Law?

SOCIAL INDUSTRIAL RELATIONS

The Biological Trend of Industry

By H. W. Jordan

Syracuse, N. Y.

As we study industry in order to chart a safe course through future years, we become deeply impressed with the fact that the trend of social, industrial life is in close accord with the laws of evolution, and that industry, to be profitable through the coming half century and longer, must avail itself of biology and the associated sciences to as great an extent as it has used physics and chemistry for its guide during the past forty years.

Engineering industry since 1880 has made huge progress by combining applied science with extreme specialization. One man used to build an entire wagon. Wagon building was a handicraft. The automobile is cut into a hundred separate machine tasks. All industry is the same. In consequence we have passed from a generalized, whole job people to a specialized, part job people.

From biology we learn that generalized species have great powers of survival, and that specialized species have steadily declining powers of survival, unless the specialization be correctly counterbalanced by coöperation. The most highly perfected social organizations are those of the ants and the bees, among whom the three vital functions of reproduction, nutrition, and housing and defense are completely specialized. Yet hill or hive life is perfect; because there is 100 per cent coöperation. No class or individual tries to seize the privileges or functions, the rights or duties of its associates. Each bee and ant does its full share of work to the utmost of its ability.

Ideal Democracy, whether of government or industry, means, not less specialization, but fuller coöperation. The science of biology, of evolution, proves that our best defense against the harmful influence of specialization is complete social industrial coöperation. Class contention, whether of labor or capital, hastens and deepens the ill effects of specialization.

It is a pleasing popular notion that the huge material progress of the last generation is to continue indefinitely. Folks think, as they did in the fur coat and silk shirt days of the war, that there can be no end to the almost vertical material advance. But as Professor E. G. Conklin recently said in "The Direction of Human Evolution," a book from which every American business executive and engineer can gather knowledge of profound value: "Again and again in the evolution of animals and plants extreme specialization in certain lines has brought about rapid progress, but has led to a lack of stability and adaptation and has ended in extinction. There is good reason to believe that the same is true of the evolution of human society. Extreme development of ideals of organization and efficiency or of liberty and equality, leads to an unbalanced state of society. Stable progress consists in advance along coöperative lines."

The rushes of advance by specialization are correctly represented by the upper half of a parabola. The parabola rises at first almost vertically, then swings over into an approximation to the arc of a circle, and flattens finally into a line almost horizontal. Now, in 1921, we are started on such a horizontal line of material, industrial development. The wonder days are over. We must lay our fur coats and silk shirts away in tar paper with moth balls, and settle down on a straightaway course of industrial plugging. Material, industrial progress has become static.

When one movement in evolution becomes static, a new movement surges up. It is clear that the evolution that will occupy us the next half century is of democracy; democratic expression of the mind in government, society, and industry. And that if we provide guidance in accordance with the constructive phases of evolution, the movement will lay an orbit of constructive coöperation. But if we say it is no affair of ours, and permit matters to drift, the result will be the steady decline which experience proves inevitable. "Insistence on personal freedom and on the rights of individuals has gone far toward weakening the bonds of union and destroying coöperation," says Conklin. "Unquestionably the further evolution of society must lie in the direction of greater coöperation, and any system of organization which exalts individual freedom to the detriment of social union and harmony must go under in the struggle for existence. The greatest problem which confronts all types of government is the problem of social coöperation. It was the failure of coöperation rather than of specialization which led to the downfall of almost every great civilization of the past, and it is this danger especially which confronts the modern world.

"We are finding that the pioneer ideals of personal liberty and independence are incompatible with the requirements of a populous country and a well-organized society. Personal freedom must be subordinated more and more to social freedom, and pioneer society must give place to the more highly organized state in which increased specialization and coöperation are the companion principles of progress."

If we pay proper heed to our duties, by doing unto others as though we were the others, our rights will fall into correct order of themselves. Coöperation is the new freedom that July 4, 1921, brings to us.

A NEW SOCIAL INDUSTRIAL CONSCIOUSNESS IS SPRINGING UP from various sources and many lands. It is the consciousness that the trend of human social relations is in strict accord with the laws of biology. And that if we would correct many of our present social difficulties and avoid greater ones in the future we must apply the laws of biology and evolution to industry in its relations to individual, community, and national life, as steadily and persistently as we have applied chemistry to the evolution of the steel industry or physics to the automobile and aviation.

Among the more important of these recent discussions of industrial biology are the writings of Professor Edwin Grant Conklin of Princeton, who is quoted above. *Scribners' Magazine* of March contained "Some Biological Aspects of Immigration," by him. And his book, "Heredity and Environment in Development of Man," preceded "The Direction of Human Evolution," from which we have quoted.

"FUTURE MAXIMUM POPULATION OF THE UNITED STATES," an article by Professor Raymond Pearl in *Harpers' Magazine* for May is a similar biological study. He predicts that maximum to be about two hundred million people, or less than twice the present population; and that this number will be reached in about one hundred and eighty years. His figures are confirmed by Professor East of Harvard in the June *Scientific Monthly*.

The *Atlantic Monthly* of June contains an article on biology by Vernon Kellogg, and one on "Industrial Development of Undeveloped Countries," by Bertrand Russell, an English authority, both of which present certain phases of industrial evolution. Many other such citations to current literature could be made, but these are sufficient to prove the wide growing conviction that government, commerce, and all social trend are manifestations of biology in human evolution.

FIFTY YEARS AGO, OR LESS, WE BEGAN TO EDUCATE and to train chemists and engineers to apply science to material things by research and experimentation. To-day the processes and machines that sprang from that applied science are operating as well as, or better than, before the war. It takes the same number of pounds of coke to produce a ton of pig iron as it did in 1913. A pound of coal evaporates the same pounds of water to steam.

The records of history indicate that the vocations of buying and selling, government, and of all that which we call social life were already well started some four thousand years ago in Egypt, Babylonia, Phoenicia. In 1921 pretty nearly every one of those ancient social activities is in a bad way and getting worse. The methods of organizing and directing them have not produced standardized results or dependable reactions.

We chemists and engineers got a late start. But when it comes to comparing results on the basis of the degree of perfection attained, we appear to have beaten the social directors by several lengths. So, why not try out our methods, by applying biology and associated sciences in research and experimentation upon small, typical social groups, as an effort to evolve a fairly well perfected society, in the next fifty years?

....

Spare Time

Editor of the Journal of Industrial and Engineering Chemistry:

After reading your editorial note that Dr. Jordan would continue to write on "Social Industrial Relations," I was shocked at Mr. Sprague's criticism of Jordan's earlier contribution, "Spare Time." It is futile to answer Mr. Sprague because his criticism simply does not apply to the article in question. Since Mr. Sprague questions the place of "Spare Time" in our JOURNAL, I feel that it may throw some light on its pertinence to tell why I, as a chemist, personally took it to heart and have sought to remedy a difficult position along the lines indicated in "Spare Time." I have spent the 18 years representing the entire time I have been out of college in a highly specialized industry having only 4 factories in the country. The managers of these factories do not look in a friendly way on immigrations from one plant to another. The specialized knowledge which one gains in this industry is of little value to any other industry. It makes one realize the truth of Jordan's statement that when specialization goes so far that it fits us to do only one thing, we lose our self-reliance.

I cannot help but think that Mr. Sprague's complacent attitude is founded on his confidence in an impregnable financial position. "If" he had to consider beginning again with worn-out tools he might see more merit in Jordan's point of view.

C. M. JOYCE

LEOMINSTER, MASS.
June 11, 1921

SCIENTIFIC SOCIETIES

Local Sections Protest against Industrial Alcohol Restrictions

That the chemists of the country are thoroughly aroused to the dangers of further restriction of the use of alcohol for legitimate industrial purposes in an endeavor to enforce the Eighteenth Amendment of the Constitution by means of a law more stringent than the original Volstead Act, was clearly demonstrated in the papers read and the sentiments expressed at various local section meetings, held during the month of June, which were given over entirely to the discussion of this vital subject.

The New York Section held a meeting on June 10, the Philadelphia Section on June 16, and the Maryland Section on June 17, all of which were largely attended and addressed by experts in various lines of industry which would be affected by proposed legislation further to restrict legitimate uses of alcohol.

The immediate cause of protest on the part of chemists was the introduction of H. R. 5033, later amended and resubmitted as H. R. 6752, by Mr. Volstead, chairman of the House Judiciary Committee. The ostensible object of the measure is to limit the prescribing of malt liquors for medicinal purposes, but advantage has been taken of the situation to incorporate into the bill certain provisions which further restrict the use of alcohol for industrial purposes.

It was made clear by all speakers at the protest meetings that the chemists were not concerned with any legislation designed to enforce prohibition of beverage alcohol, but that they were very much concerned over any restrictions or regulations affecting industrial alcohol. That the protests have been of some value is evidenced by the fact that the Rules Committee of the House has refused to grant the request of Mr. Volstead and his followers to permit this legislation to be passed without hearings and proper debate. As a result, bills have been introduced in both House and Senate divorcing from H. R. 6752 the regulations regarding the prescribing of malt liquors and leaving that portion of the bill which affects industrial alcohol for further consideration.

The program of the New York Meeting was typical of that of the other sections, and the points brought out there in the reading and discussion of papers give a general idea of the contentions of the chemists of the country.

Chairman John E. Teeple of the New York Section brought the matter before the members in his introductory remarks as follows:

> In announcing this meeting to-night I tried to make it perfectly clear that we were not here to discuss prohibition, its advantages or its disadvantages. That is a matter of private opinion and not a subject for action by this organization of chemists. We are not here to discuss the desirability of enforcing the prohibition enforcement act or any other act on the statute books. But the prohibition enforcement act clearly distinguishes between alcohol for industrial use and alcohol for beverage use. We are vitally interested in the first form of alcohol, and, as a Society, are not at all interested in the second form.
>
> The enforcement act instructs the Commissioner to prevent the use of alcohol as a beverage. This is accordingly his duty. But just as definitely and clearly it instructs him to insure an ample supply of alcohol and promote its use in scientific research, and in the development of fuel, dye, and other lawful industries. Consequently this is also a lawful duty of the Commissioner. If the Commissioner attempts to carry out his proper function in both cases, he will of course at times meet difficulties, and will probably develop a tendency to lean toward one duty at the expense of the other in order to avoid these difficulties. The Anti-Saloon League propagandists can see only prohibition in the law or in the duty of the Commissioner. The chemist sees another duty which is just as important and just as much a matter of law; that is the duty of promoting the use of alcohol in the industries.
>
> I received a very courteous letter this morning from Mr. Wayne B. Wheeler, general counsel of the Anti-Saloon League, referring to the announcement of our meeting. He says this printed announcement gives him the impression that some of our members have been misled concerning the provisions of the pending supplemental enforcement bill, and that many of those who spoke against the bill in its original form were unduly alarmed about the possible effects of it. The bitter experiences of legitimate chemical firms of long standing who have occasion to use alcohol for legitimate purposes are a matter of record. Some of these experiences and difficulties will be related to you to-night. A little careful thought will indicate that these people, with a continued history of unnecessary interference with their business still fresh in their minds, are not likely either to be misled or unduly alarmed. They know what is happening and what will result from the present trend. They have reason to see this situation much more clearly than Mr. Wheeler could possibly see it, and at this meeting to-night the various speakers want to give you a clear picture of the situation as it exists.

Dr. Teeple cited a number of incidents to show the manner in which legitimate industries had been hampered by prohibition enforcement officers who seem to have been unable to discriminate between legitimate and illegitimate uses of alcohol.

Dr. Martin H. Ittner, chairman of the Committee on Industrial Alcohol of the American Chemical Society, next presented a paper entitled "Industrial Alcohol and Prohibition Enforcement." He related the experience of his Committee before the Judiciary Committee of the House, when they appeared to present the resolutions that had been passed by the Society, and to offer specific suggestions toward the modification of some of the more objectionable provisions in enforcement legislation then before Congress. The Committee was shown scant courtesy by Chairman Volstead and some other members of the Judiciary Committee, and had great difficulty in presenting its contentions because of the unfriendly and, at times, insulting attitude of some members of the House Committee. Dr. Ittner analyzed H. R. 5033, which has been superseded by H. R. 6752, pointing out the hardships which the former measure, and to some extent the latter, would work upon legitimate industries. The fact that H. R. 6752 has been substituted for H. R. 5033, and that it is free from several of the provisions to which the Industrial Alcohol Committee of the Society took exception, indicates clearly that the work of the Committee did not go for naught.

Dr. M. C. Whitaker, vice president of the U. S. Industrial Alcohol Company, was unable to be present at the meeting. His paper which was read by Dr. Teeple, is printed in full in this issue of the Journal (pp. 647 to 650).

Mr. W. L. Crounse, attorney of the National Wholesale Druggists' Association, related his experiences with various prohibition enforcement officials, indicating that these officials were not always possessors of the highest type of moral character, and cited various incidents to show that prohibition enforcement had been made a source of illegitimate revenue for a number of individuals holding office as prohibition officials. He attacked the methods employed by former Prohibition Commissioner John F. Kramer and Wayne B. Wheeler, general attorney of the Anti-Saloon League, as being unfair to the interests of the legitimate users of industrial alcohol.

Mr. F. M. Boyles, chairman of the Baltimore Section and chief chemist of McCormick & Company, Inc., spoke on "Industrial Alcohol and Its Relation to the Flavoring Extract and Food Industries." He stated that it was impossible to manufacture high-grade flavoring extracts without the use of alcohol, and that the delay in securing permits from the Government made it practically impossible to manufacture any but regular line products, although there is quite a demand for flavoring extracts made up according to special formulas for specific uses.

The final speaker was Hon. Alfred D. Van Buren, counsel of the Legal Division of the Internal Revenue Bureau, who spoke on the legal status of industrial alcohol and its relation to prohibition enforcement. Mr. Van Buren asserted that one could cite just as many incidents, contributed by the industries, which had tried the patience of the Prohibition Commissioner's office and the Internal Revenue Department, as had been related on the other side of the case by the representatives of industry. He stated that proper enforcement of the law could come only through a spirit of coöperation and more intimate contact of legitimate industries with the enforcement officers at Washington. In his opinion, the Government was eager to coöperate with the industries in promoting the use of alcohol for industrial purposes, but in many cases permits had been secured under false pretenses, and beverage preparations had been made and sold in clear violation of the law. He commended Mr. Wheeler and the Anti-Saloon League for the great help they had given the Prohibition Enforcement Office, and voiced his feeling that most of the difficulties now existing could be solved if physicians, pharmacists, chemists, and others interested in the legitimate use of alcohol were to get together and advise the Enforcement Officers of necessary regulations for properly securing their needs and for helping these officials to rid their own professions of those who break the law.

The program of the Maryland Section included the following papers:

"Industrial Alcohol from the Standpoint of the Manufacturer," by A A. Backhaus.

"Industrial Alcohol's Place in Chemical Industry," by A. E. Marshall.

"Industrial Alcohol from the Standpoint of the User," by A. R. L. Dohme.

"Industrial Alcohol and Prohibition Enforcement," by Richard H. Bond.

The program of the Philadelphia Section included a paper by Prof. Charles H. LaWall on "The Impotance of Industrial Alcohol to the Pharmaceutical Industry."

Detroit Meeting of the American Institute of Chemical Engineers

The Thirteenth Semiannual Meeting of the American Institute of Chemical Engineers held in Detroit, Michigan, June 20 to 25, 1921, was a pronounced success from beginning to end. The efficient local committee met the New York delegation at the D & C steamer landing with a large sightseeing bus which conveyed the party to the Statler Hotel, where the meeting opened almost immediately with an attendance of about 100.

At the business session the Secretary reported a membership of 515, a gain of 100 during the year. Reports of the council, officers, and committees showed active work since the last meeting. Baltimore, Md., was chosen as the meeting place for the winter convention. President Wesson, in his address, showed how, through its committees, the Institute is active, in an ever-increasing range of interests which vitally concern the chemical engineer.

The main feature of the program of papers was a symposium on the Automotive Industry. The leading technical men in this important industry had contributed papers showing the best practice to-day, as well as the lines along which developments may be expected.

Dr. C. D. Holley, director of research, Acme White Lead & Color Works, opened the symposium with a paper on "The Manufacture and Application of Automobile Finishes." Dr. Holley discussed the materials used in automobile finishes, and the most improved methods of application and drying, as well as improved methods of manufacture of paints and varnishes.

Mr. G. C. Given, of the Atlas Powder Co., Stamford, Conn., discussed the manufacture of pyroxylin artificial leather. Numerous samples of the product in various stages of manufacture helped to make the subject clear to the audience. Mr. Wm. M. Corse, general manager, Monel Metal Products Corp., gave a resumé of the most important properties of this very valuable metal. Samples of golf stick heads made of monel metal were shown.

The gasoline situation was discussed by E. H. Leslie, associate professor of chemical engineering at the University of Michigan. Increased cost of motor fuel was predicted on the one hand, while Mr. O. C. Berry, chief engineer of the Wheeler-Schebler Carb. Co., showed very graphically and clearly that with the present wasteful method of utilization of gasoline it was easily possible to design and operate heavy cars at 40 miles per gallon, thus neutralizing the high cost of fuel per gallon.

Mr. Wm. G. Nelson, chemist, with Morgan & Wright, described the various factors which shorten the life of a pneumatic tire.

A. H. Blanchard, professor of highway engineering and highway transport, University of Michigan, called attention to a number of important problems in highway engineering which could be solved by the chemical engineer.

Dr. J. H. Ransom, chief of research, Michigan Smelting & Refining Co., in a paper on "Some Problems in Nonferrous Metallurgy," pointed out important lines of research in this field, while Prof. A. E. White, director of the Department of Engineering Research, University of Michigan, gave similar information with reference to iron and steel.

W. A. Gatwood, engineer, Hoskins Mfg. Co., read a paper on "Heat Treatment of Steel."

W. B. Stout, chief engineer, Stout Engineering Laboratories, read a very interesting paper on "The Future of Aeronautics," in which he predicted a rapid increase in their use for both commercial and pleasure uses.

Very great interest was shown in a paper by R. S. Tour, chief engineer, Second Nitrate Division, Ordnance Dept., Washington, D. C., on "German and American Haber Synthetic Ammonia Plants." The author gave very full details, including drawings of the German plants for the production of synthetic ammonia, as well as yields and cost of installations. He also discussed very fully the plant at Sheffield, Ala., and pointed out the serious defects in the design of this plant which prevented its being operated.

A very complete resumé of the glue industry was given by Ludwig A. Theile in a paper on "Evolution of the Glue Industry and Grease Extraction."

E. M. Baker of the University of Michigan, in collaboration with V. H. White and A. R. Carr, presented the results of a study of the boiling points of salt solutions at reduced pressures, and showed how if two boiling points were known others could be calculated.

The plant inspections included the large new plant of the Cadillac Motor Co., the plant of Hiram Walker & Sons, Ltd., Walkerville, Ont., and the Ford River Rouge plant. The last proved to be a very well-built modern plant which was operating at capacity. Some twenty other plants were listed, many of which were visited on Friday and Saturday by small groups of the chemical engineers.

A large delegation took the steamer trip on Friday to St. Clair, Michigan, and visited the plant of the Diamond Crystal Salt Co., where the Alberger and Grainer process was in operation, producing a salt which is almost absolutely free from calcium and magnesium salts. Special interest was shown in the heaters, in which the brine is heated to 280° C. and the calcium sulfate is precipitated out as a hard scale which is drilled out at frequent intervals.

The speakers at the subscription dinner on Thursday evening at the Hotel Statler were Henry M. Leland, president, Lincoln Motor Co.; Chester M. Culver, manager, Detroit Employers' Association; J. C. Olsen, secretary, and David Wesson, president, American Institute of Chemical Engineers; Chas. T. Bragg, works manager, Michigan Smelting & Refining Co.; and Capt. Lucius E. Allen, consulting and constructing engineer, Belleville, Ont., Canada.

The entire day, Tuesday, June 21, was spent at the University of Michigan at Ann Arbor. The morning was spent in visiting the laboratories, while the afternoon was devoted to the reading and discussion of technical papers. In a very elequent address at luncheon at Michigan Union, President M. L. Burton emphasized the special service which the State University can render to the Republic.

J. C. OLSEN, *Secretary*

POLYTECHNIC INSTITUTE
BROOKLYN, N. Y.

National Lime Association Holds Annual Convention

The Third Annual Meeting of the National Lime Association took place at the Hotel Commodore, New York, June 14 to 17, inclusive. Over one hundred lime producers from various sections of the country were in attendance.

In opening the meeting, President Charles Warner called attention to the program of the National Lime Association which includes the building up of a strong technical staff to handle the educational and technical work of the industry. He pointed out that the industry was greatly in need of research work on lime and its uses, and that this work will be carried out in the laboratory of the Association, as well as by the creation of ships in government institutions and universities.

The work of the convention was divided along three principal lines, including a symposium on lime production problems, a series of papers and discussions on the subject of extending the use of lime, and finally the actual business sessions which included reports of officers and department heads.

In the symposium on lime production problems, the following papers were presented:

Some New Features in Lime Kiln Construction. RICHARD K. MEADE.

Chemical Control, the Key to Kiln Efficiency. W. D. MOUNT.

The Fine Art of Lime Burning. GEORGE B. WOOD.

Standardization: Government Research and Industrial Development. S. W. STRATTON, Director, U. S. Bureau of Standards.

Problems to Be Considered in Changing a Quarry from Hand Methods to Steamshovel Methods. IRVING WARNER.

Relations of Banking Institutions to Social Service. WILLARD A. ECKMAN.

Social Service Applied to the Lime Industry. E. J. HEIMBERDINGER.

In the symposium on extending the use of lime, the papers presented were:

Ready Mixed Wet Mortar. W. C. HAY.

An Architect's View of Lime and Its Use. D. K. Bloyd.

The Dependence of the Lime Industry on Nature and Science. Arthur D Little.

Getting Facts about Lime in the Soil. W. H. MacIntire.

The Use of Lime in Water Purification. C. R. Brown.

At the business session of the Association reports were made by General Manager E. O. Fippin and the department managers, who are L. H. Hart, in charge of construction, M. E. Holmes, in charge of chemistry, and J. A. Silpher, in charge of agriculture.

The following resolution was unanimously adopted by the Association:

> Whereas, A complete, self-sustained coal-tar chemical industry is essential to the industrial development of our country, to its national safety and security, and is important in its very close relation to medical science, and
>
> Whereas, It has been shown that unusual protection must be given by the government to this industry, the development of which began only when the war gave it its opportunity, and that a tariff alone will not protect it adequately against the determined assaults of the German-government-fostered-chemical-cartel which is seeking to regain this, the world's richest market, now the only market without permanent protection,
>
> *Therefore, be it resolved,* That the National Lime Association hereby urges upon Congress in solemn earnestness the prompt enactment of adequate legislation to protect and maintain in this country this vital chemical industry.

Seventh National Exposition of Chemical Industries

Plans for the Exposition to be held during the week of September 12 to 17 at the 8th Coast Artillery Armory, New York, following immediately the meeting of the American Chemical Society and of the Society of Chemical Industry, are progressing apace. The number of exhibitors is increasing, and work on the exhibits is reported by exhibitors to be well under way. The managers report that considerable interest is being shown among men in the various industrial fields, and a record attendance is expected.

In the auditorium, which is a brick fireproof structure in the building, the program of papers will be given, and motion pictures will be shown. The plans include symposiums on chemical engineering subjects: one on Evaporating and Drying, another on Crushing, Grinding and Pulverizing, a third on the Power Plant in the Chemical Industries. Other subjects will be discussed and fuller details of the program will be given in the next issue of This Journal. At present the following papers are included on the Crushing, Grinding and Pulverizing program:

Ball and Pebble Milling for Pulverizing and Mixing. H. F. Kreinfeldt, Abbe Engineering Co.

Grinding and Pulverizing with Air Separation. S. B. Kanowitz, Raymond Bros. Impact Pulverizer Co.

Crushing and Grinding Phosphate Rock. L. H. Sturtevant, Sturtevant Mill Co.

Dust Collection as Applied to Grinding and Pulverizing Problems. M. I. Dotfan, Allis-Chalmers Mfg. Co.

Upon the Evaporating and Drying program the following will appear:

(Subject to be announced.) E. G. Rippel, Buffalo Foundry & Machine Co.

The Relation of Atmospheric Conditions to Chemical Processes. A. E. Stacey, Jr., Carrier Engineering Corp.

Drying and Drying Problems. H. S. Landell, Proctor & Schwartz.

Special Problems for Enameled Evaporators. Max Donaeur. Elyria Enameled Products Co.

Drying with Moist Air. Arthur B. Stonex, Hunter Dry Kiln Co.

Drying as an Air Conditioning Problem. A. S. Lissauer, W. L. Fleisher & Co. Inc.

Atmospheric Drying by Means of Compartment, Tunnel and Continuous Belt Conveyor Dryers with Some Practical Applications. J. D. Stein, Grinnell Co., Dryer Division.

Spray Drying. W. H. Dickson, Atomized Products Co.

Evaporation. H Austin, Ernest Scott & Co.

Papers on the Power Plant in the Chemical Industries include:

Modern Boiler House Arrangement and Equipment. R. M. Gordon, The Solvay Process Co.

Suggestions for Reducing Heat Losses in Chemical Plants. John Primrose, Power Specialty Co.

Boiler Feed Water Treatment and Treatment Control. E. G. Bashore, Rice & Bashore.

Under the head of Industrial Problems will be several papers, among which are:

Solvent Extraction of Edible Fats and Oils. H. Austin, Ernest Scott.

The Limitations of Silent Chain Drive. F. G. Anderson, Morse Chain Co.

The motion pictures at the Exposition will cover nearly every phase of the chemical industries, as indicated by the following list. The Bureau of Mines is sending some 25 subjects for this program.

Chemical Industries

The Story of Sulfur. (2 reels) Courtesy of Texas Gulf Sulphur Co.
Making Soap. (1 reel) Courtesy of Baumer Films.
Manufacture of Dynamite. (1 reel)[1]
Manufacture of Pyrex Glassware. (3 reels) Courtesy of Corning Glass Co.
Manufacture of Portland Cement. (2 reels)[1]
The Jewels of Industry. (8 reels) Courtesy of The Carborundum Co.
  (*a*) **Creating Power from Water.**
  (*b*) **Within the Power Plant at Niagara.**
  (*c*) **In and About Niagara Falls.**
  (*d*) **Power at Work in the Carborundum Plant.**
  (*e*) **Making the Crystal Masses in the Electric Furnace.**
  (*f*) **And Making Them into Stones, Grinding Wheels, Paper and Cloth.**
  (*g*) **Usual and Unusual Uses for Abrasives in Some Fifty Industries.**
The Electric Heart—the Dry Cell. (1 reel) Courtesy of Baumer Films.
Canning Electricity—the Wet Cell. (1 reel) Courtesy of Baumer Films.
The Making of Oleomargarine. (1 reel) Courtesy of Armour & Co.
The Manufacture of Dry Sausage. (2 reels) Courtesy of Armour & Co.

Mining and the Chemical Industries

The Story of Rock Drilling. (4 reels) Courtesy of Sullivan Machinery Co. and U. S. Bureau of Mines.
Iron Mining Operations. (4 reels)[1]
  (*a*) **Stripping.**
  (*b*) **Exploration and Stripping.**
  (*c*) **Underground Mining.**
  (*d*) **Logging Operations.**
Mining Magnetic Iron Ore. (2 reels)[1]
Zinc Mining, Milling and Smelting. (4 reels)[1]
Manufacture of Zinc Oxide. (1 reel)[1]
Mining and Extraction of Radium from Carnotite Ore. (2 reels)[1]
Mine Explosion and Rescue. (1 reel)[1]
Exterminate the Mosquito. (1 reel)[1]

Handling of Material

Saving Wasted Millions through Material Handling Equipment. (2 reels)[1] Courtesy of Economy Engineering Co.
Use of the Steam Shovel in Mining. (1 reel)[1]
Transportation and Storage of Iron Ore. (1 reel)[1]
Transporting and Handling Coal by Various Means. (1 reel)[1]
Dredging Anthracite Coal. (1 reel)[1]

The Power Plant

Conserving Coal and Saving Heat Values by Insulating Steam Pipes and Boilers. (1 reel) Courtesy of Magnesia Association of America.
The Cost of Careless Firing. (2 reels)[1]
Getting the Most Out of Coal. (1 reel)[1]

Calendar of Meetings

Society of Chemical Industry—Annual Meeting, Montreal, Canada, August 26 to 31, 1921.

American Chemical Society and Society of Chemical Industry—New York, N. Y., September 6 to 10, 1921.

Seventh National Exposition of Chemical Industries—Eighth Coast Artillery Armory, New York, N. Y., September 12 to 17, 1921.

American Electrochemical Society—Fall Meeting, Lake Placid Club in the Adirondacks, N. Y., September 29 to October 1, 1921.

---

[1] These films by courtesy of U. S. Bureau of Mines.

NOTES AND CORRESPONDENCE

Cooperative Analytical Work of the American Oil Chemists' Society

Editor of the Journal of Industrial and Engineering Chemistry:

The system of collaborative work on the analysis of meals, formerly known as check meal work, which has been under operation in the American Oil Chemists' Society for the past six years, is to be conducted this year on a greatly enlarged scale.

The main object of this collaboration is to provide a reliable means whereby chemists may discover tendencies of their laboratory organization to deteriorate in the accuracy of the work done, and may locate and eradicate the causes.

This season the work will deal with four groups of samples: meals, feedstuffs, or allied materials; fertilizers; fats; and crude oils.

The meal series, to be analyzed for moisture, oil, and ammonia, will consist of forty samples which are to be reported weekly, beginning August 8. These samples, it may be added, will include high protein wheat flour, linseed meal, brewers' grain, beet pulp, cottonseed meal, peanut meal, soy-bean meal, etc. The fertilizer series will contain eight samples, to be reported monthly, beginning September 19. Six fat samples will be issued, each to be analyzed for one or more constants. These are to be reported monthly, beginning September 5. In the crude oil group, two samples of cottonseed and one of peanut oil will be issued for refining tests.

All tests on fertilizers and fats are to be made strictly in accordance with specific directions. With the crude oils, the method of refining will be defined, and the strength of lye prescribed. The methods for determination of oil, ammonia, and moisture on meals will be left to the discretion of the analyst, provided the major details comply with the Official Rules.

As in previous years a laboratory cup will be awarded to the analyst whose total average efficiency on the entire forty meal samples, for both oil and ammonia, is highest. At the close of the series, accuracy certificates will be awarded for meritorious work in the various groups.

The work is open to any interested chemist, whether he be a member of the Society or not. It should appeal specially to the various types of feed and food chemists. A number of State and Federal chemists have been included among the collaborators in the past. During the past year, 107 chemists took part in the work.

Federal and State chemists may obtain any or all of the series free of charge. Members of the American Oil Chemists' Society will be allowed a discount of 25 per cent on the prices listed in the bulletin issued by the Society. The bulletin also gives details as to the distribution and handling of samples and methods of calculating accepted averages and of rating work, and also includes a list of dates before which reports of results must be in the hands of the chairman.

F. N. SMALLEY, *Chairman*

THE SOUTHERN COTTON OIL CO.
SAVANNAH, GEORGIA
June 6, 1921

The Volumetric Determination of Aluminium in Its Salts—Correction

In my paper on the above subject [THIS JOURNAL, **13** (1921), 420] certain errors, typographical and otherwise, escaped my correction.

In Table II, "0.27 N" should read "0.2$\dot{7}$ N." Similarly in Table VII, column 4, "0.27" should be "0.2$\dot{7}$" for the samples II to VI, inclusive.

The opening paragraph is too sweepingly phrased, since the opinions expressed are based partly on unpublished (and therefore uncriticized) work. I ask leave to insert "alone" before "is useless" in line 2, "prime" before "importance" in line 5, and "essential" before "part" in line 8.

ALFRED TINGLE

E. B. EDDY CO., LTD.
HULL, P. Q., CANADA
June 25, 1921

Civil Service Examinations

The United States Civil Service Commission has announced examinations for Valuation Aid at $1200 to $2500 a year, Assistant Valuation Engineer at $2500 to $3600 a year, and Valuation Engineer at $3600 to $4800 a year, with higher salaries in exceptional cases. Appointees at $2500 or less may be allowed the increase of $20 a month. Vacancies in the technical staff of the Income Tax Unit of the Bureau of Internal Revenue and similar positions will be filled from these examinations. The duties will involve the estimation of (1) the quantity of oil and gas or timber, (2) the theoretical and market values of oil and gas in place of standing timber, and their products, (3) the value of equipment ordinarily used in the discovery, exploitation, and utilization of such natural resources, and (4) the cost of development, exploitation, and utilization of natural resources. In addition, a general knowledge of the processes and conduct of the industry will be required. Separate registers of eligibles will be established for (1) oil and gas, and (2) the forest industry. Competitors will be rated on (1) physical ability—10 points, and (2) education, training and experience—90 points. Applications will be rated as received until September 1, 1921.

The Commission has also announced an examination for Assistant Metallurgical Chemist on August 17, 1921, to fill vacancies at the Naval Ordnance Plant, South Charleston, W. Va., at $5.44 per diem, and similar positions. The duties of appointees will consist of analysis of steel, iron, alloys, and other metallurgical materials, and will require ability to make quick test analysis of steel for the following elements: carbon, silicon, manganese, sulfur, phosphorus, nickel, and chromium. Candidates will be rated on general chemistry and physics, metallurgical chemistry, and education and experience. Applicants must be high school graduates and must have had either two years' college training which included chemistry, physics and metallurgy, or at least one year of practical laboratory experience in the analysis of metals and metallurgical materials.

Utilization of Niter Cake

At the May meeting of the Manchester (England) Section of the Society of Chemical Industry, W. H. H. Norris outlined recent progress in the utilization of niter cake. Before 1915 niter cake was utilized in England to only a very small extent, and even with the increased production during the war over 80 per cent was used by methods which completely wasted the sodium sulfate content. The process of using niter cake for ammonia absorption was described. By this method 220 tons of niter cake are used for the production of 157 tons of salt cake and 87 tons of ammonium sulfate, the apparatus being run in conjunction with a Mond gas ammonia recovery plant. The process is of wide application and may be used either with ammonia absorption towers and dasher washers, or in the ordinary saturator as employed on coke ovens and gas-works liquor recovery plants. The operation works up its own waste liquors and requires a minimum of handling and evaporation. The niter cake is digested with heated process liquor, and the whole of the salt-cake content is precipitated in pure form, while the acid is taken into solution. The mixture is filtered and washed in centrifugals, and the resulting acid liquor is used for ammonia absorption. From the neutralized liquor, ammonium sulfate containing over 24 per cent ammonia is deposited, but when a definite density is reached the process liquor is run back to the digester to be used with a fresh charge of niter cake.

WASHINGTON LETTER

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

Congressional activity of interest to chemists now centers in tariff and prohibition legislation, with alcohol as the chief ingredient.

THE INDUSTRIAL ALCOHOL SITUATION

Attempts to strengthen the National Prohibition Act so as to allow more effective enforcement of liquor legislation resulted in wording of the supplemental bill which endangered the supply and production of pure alcohol, which is now indispensable in drug and chemical manufacture. The first bill, H. R. 5033, introduced by Mr. Volstead, provided that the commissioner of internal revenue should limit the supply and use of all liquors to the actual needs for nonbeverage use, and should grant only the permits which in his judgment were necessary to supply such needs. It also provided that if an intoxicating liquor other than alcohol were used in the manufacture of drugs and medicines it should have added to it a component part of the finished article so as to render it unfit for use for intoxicating beverage purposes. The bill also provided for dual control by the commissioner and the Attorney General. After hearings at which many chemists and drug manufacturers recited the harm that would be caused by these provisions, the Committee on Judiciary drew up a new bill, H. R. 6752, as a substitute measure. This omitted the requirement that a part of the component material must be added to alcohol at the distillery, but still provided that the commissioner should grant only the permits that were necessary to supply the actual needs for nonbeverage purposes and should limit the supply and use of all liquor save denatured alcohol and denatured rum unfit for internal use to such nonbeverage needs. It does state, however, that "this provision shall not authorize the commissioner to limit the quantity of alcohol that may be manufactured, nor shall it be taken to repeal the right of the applicant for a review of the decision of the commissioner in refusing a permit by a court of equity as provided in the National Prohibition Act." Even with this limiting clause, those who use industrial alcohol declare that this provision destroys the one essential safeguard to chemical industry and national welfare assured by the National Prohibition Act which was passed "to insure an ample supply of alcohol and promote its use in scientific research and in the development of fuel, dye and other lawful industries," as well as to prohibit intoxicating beverages. The language proposed would give the commissioner power to dominate every industry using alcohol by regulating the supply and use thereof, and consequently would affect the price of the commodities concerned, they believe. Hearings will be held on the revised bill, which has been favorably reported to the House, and the chemists interested will have a chance to point out the possible dangers.

THE EMERGENCY TARIFF ACT

The Emergency Tariff Act has been signed by the President and is now in force. It became a law with no essential changes, so far as dyes and chemicals are concerned, except that the period of control by license was reduced from six to three months, although the tariff portion of the Act was made effective for the full six months. Work on the regular tariff bill has progressed to the point that the main committee is considering the recommendations of the various subcommittees of the Committee on Ways and Means that have been formulating the different schedules. No information is being given out as to the rates being considered, and detailed information will not be available until the bill is reported to the House, probably about July 1.

The Tariff Commission will issue early in July its annual volume on "Census of Dyes and Coal-Tar Chemicals" which will give quantities and values of these chemicals during 1920.

ARMY APPROPRIATION BILL

The Army Appropriation Bill is now in conference, and there seems to be little chance that the Chemical Warfare Service will receive more than the $1,350,000 that was decided upon previously. Chemical Warfare officers are disappointed because their recommendations that poison gas as well as high explosives should be used in the air-warfare tests between the Army and the Navy were disapproved. Officer personnel of the Service has been increased until it is nearly up to the strength provided for by law. (There are at present about 90 officers, and 100 are authorized.) The Service is manufacturing at its plant at Edgewood chemical warfare materials for the Navy, which has no plant of its own. At present, gas masks are being made.

PATENT OFFICE

The bill providing higher Patent Office salaries has just been reported favorably to the House. This measure has practically the same provisions so far as salaries are concerned as the bill which failed last session after passing both House and Senate. Chances for early favorable action on the patent bill are said to be good, and the passage of this measure will begin to relieve the Patent Office situation. In spite of the business depression, according to Commissioner Robertson, the Patent Office did the largest business of its existence during the month of May.

An amendment to the revised statutes providing that any patents issued to foreigners must be put into operation, and that, within two years production in reasonable quantities must be begun within the continental limits of the United States, has been proposed by Senator Stanley of Kentucky. This legislation is intended to prevent foreign monopolies of dyes and other complex chemicals, such as occurred at the beginning of the war when German interests held more than one thousand coal-tar patents in America but did not produce here. Nearly every other country has laws compelling production within the country of articles that are patented by foreigners.

DEPARTMENT OF COMMERCE

Of interest to those chemical industries that expect to do an export business, is the passage of appropriations that will enable the Bureau of Foreign and Domestic Commerce to establish twelve divisions that will obtain information for, and aid the various export industries. One of the twelve divisions will care for chemicals and allied products, while other divisions will be devoted to lumber, including wood products and paper, leather, machinery, iron and steel, and coal and oil. There may be a division on foodstuffs, and the remaining branches to be covered have not yet been definitely decided. Each of these divisions will have two experts in charge, and the plan proposed is that one shall be in the field while the other is in the office in Washington, and that they shall alternate from time to time. This new plan for aiding industry has been inaugurated by Secretary Hoover, and each division will have an unofficial advisory committee organized by the industry to guide the work. These divisions will be organized by July 1 or shortly thereafter.

Secretary Hoover is being aided in his work of reorganizing the Department of Commerce by F. M. Feiker, formerly vice president and chairman of the editorial board of the McGraw-Hill Co., who has accepted the task of supervising the Bureau of Foreign and Domestic Commerce, the Census Bureau, and the Bureau of Standards. His title is Assistant to the Secretary.

President Harding has appointed Dr. Julius Klein director of the Bureau of Foreign and Domestic Commerce. At present Dr. Klein is at Harvard University as professor of Latin-American history and economics, but up until last fall he was with the Bureau, serving as chief of the Latin-American division and as commercial attaché in Argentina.

Other appropriations have been secured by Mr. Hoover for the Department of Commerce which will aid the chemical industry, indirectly if not directly. The Bureau of Standards has been given $100,000 for "technical investigation in coöperation with the industries upon fundamental problems involved in industrial development following the war, with a view to assisting in the permanent establishment of the new American industries developed during the war," and another $100,000 has been made available, so that the Bureau of Standards can "coöperate with government departments, engineers, and manufacturers in the establishment of standards, methods of testing, and inspection of instruments, equipment, tools, and electrical and mechanical devices used in the industries and by the Government, including the practical specification for quality and performance of such devices and the formulation of methods of inspection, laboratory, and service tests."

BUREAU OF CHEMISTRY

The appointment of a director of the Bureau of Chemistry of the Department of Agriculture to succeed Dr. Carl L. Alsberg, who resigned to take the directorship of the Food Research Institute of the Leland Stanford Junior University, has not yet been made, but is expected in a few days.

The Bureau of Chemistry is preparing to resume its work on grain dust explosions, as appropriations for this use become available with the beginning of the new fiscal year.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Dr. F. G. Cottrell, chairman of the division of chemistry and chemical technology of the National Research Council, has sailed for Europe as one of the delegates to the meeting of the International Union of Pure and Applied Chemistry, which is to be held at Brussels the latter part of this month. Prof. James B. Conant of Harvard and Dr. Hugh S. Taylor, professor of physical chemistry at Princeton, are additional American delegates who are traveling toward Europe. Dr. E. S. Chapin and D. Collin McCall, who complete the delegation from the United States, are already in Paris. The meeting will consider the following questions: international patents, the organization of an international commission on atomic weights, reformation of the chemical nomenclature, the formation of an international laboratory for the analysis of food products, hygienic conditions of labor in the chemical industry, and the establishment of an international institute on chemical standards. While in Europe, Dr. Cottrell will also make a survey of the use of helium in European countries, and he will study the methods of oxygen separation and concentration. In this work he is representing both the National Research Council and the Bureau of Mines.

Representatives and senators have had a chance to study chemistry during the past few weeks. The National Research Council and the Chemical Warfare Service set up in the office building of the House an exhibit showing the way in which coal-tar products are used in drugs, medicines, perfumes, explosives, and poison gas. Actual samples of both the crude and the finished products were shown, and the methods of manufacture were shown by models and graphically. This exhibit has now been transferred to the National Museum, where it will be permanently installed.

MME. CURIE IN WASHINGTON

Mme. Curie's visit here and the presentation to her of America's gift, the gram of radium, by President Harding, were notable events of the end of May. While Mme. Curie was here she was honored at a meeting at which Dr. R. A. Millikan told the story of her discovery of radium and discussed the present knowledge of that substance. Mme. Curie also talked with chemists and physicists of the Bureau of Standards about her work, and officially June 15, 1921, opened the new cryogenic laboratory of the Bureau of Mines.

June 15, 1921

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

The French press is enthusiastic over the welcome accorded Mme. Curie in the United States, and the chemists of France are specially proud of the flattering words with which President Harding welcomed Mme. Curie.

At the same time, the Prince of Monaco, who has done so much for physical, chemical, and biological research in the realm of oceanography, has come back to France after his stay in the States. In a speech before the Academy of Sciences, of which he is a member, the Prince said: "The love of science is greatly honored in the United States, and obviously it is increasing under the impulsion of many remarkable men who are closely in touch with all classes of society. To-day, all Americans are united in a single thought, which groups the founders of the American republic together with the living remembrance of Lafayette." The Prince of Monaco ended by affirming not only the scientific, but also the sentimental, solidarity of France and the United States.

These two manifestations are a precious comfort for French scientists, and it is to be desired that manufacturers, as well, may come into closer communication. We should like to see groups of American manufacturers, specializing in a given industry, come to France to visit similar factories here.

I know that in America there is an important ceramic society. I happened to meet it in Pittsburgh in February 1919, at the time of its annual meeting. The English Ceramic Society has just made a survey trip to France; in Lorraine it visited the different installations of Sarreguemines, Seltz, Soufflenheim, and Altkirch, as well as several ceramic works in the Paris district. I have no doubt that American ceramists could make the same survey trip, which certainly would interest them.

MANUFACTURE OF WINDOW GLASS

The window glass industries in France are to-day in a period of transformation, and manufacturers are hesitating between the American process of the Libbey-Owens Sheet Glass Company of Toledo, Ohio, and the Belgian process of Fourcault.

The English concern, the Window-Glass Company, who held the monopoly of the Fourcault process, owned a large factory near Châlon-sur-Saône, in Burgundy, in which the biggest glass furnace existing in Europe was operated. Since production exceeds consumption, stocks are accumulating, and these works have been closed.

It is claimed here that the American process would be preferable because it would yield a cheaper product. The difficulty which occurs to engineers lies in the fact that in the States natural gas is used for heating. This gives a very steady and permanent heat, which could not be obtained with furnaces heated with coal.

The glass made by the two processes seems to possess similar qualities, but the Libbey-Owens machine seems to give a better yield.

ALUMINIUM WEEK

In an attempt to popularize the use of aluminium, magnesium, calcium, and sodium, and especially to interest investigators and manufacturers in the development of new uses, the Société d'Encouragement pour l'Industrie Nationale (Society of Encouragement for National Industry) declared an "Aluminium Week" in May.

Various lecturers dealt with the use of the light metals in alloys, in electric apparatus, in the fermentation and dairy industries, in chemical industries, and in aviation. These lectures will appear in the *Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* At the same time a very complete exhibition allowed the public to examine the apparatus about which the lecturers had spoken.

THE ALSATIAN POTASH INDUSTRY

The Potash Commission of the French Parliament has definitely settled the Alsatian potash statute.

The potash district of Alsace-Lorraine is divided between four different companies, which, with the Société Sainte-Thérèse, make five working companies. This does not seem especially desirable, for these companies, not having any unity of action, can be competed with easily by the German Potash Syndicate.

This Potash Syndicate, which controls all the German potash, including the Stassfurt district, is considering the possibility of once more taking possession of the world market. It estimates that, alone, it could easily compete with the five French companies, which necessarily have less developed means of working than it has, and it hopes rapidly to be able to take possession of the American and English markets.

It is certain that the sacrifices made by the French potash manufacturers for the home consumption should be counterbalanced by profits obtained from export, and, under these circumstances, it is obvious that the German Syndicate can hope to compete with us. Be that as it may, such competition will cause a lowering of the price, by which consumers will profit.

At the present time, the consumption of potash fertilizers in France is considerable. The pre-war consumption of K_2O was 37,000 tons; in 1920 it was 85,000 tons, and at the end of 1921 it will reach 100,000 tons. On the other hand, the consumption of phosphates, nitrates, and nitrogenous fertilizers is said to be, if not decreasing, at least on the same scale as that before the war.

THE DYE INDUSTRY

We are now getting information about the comparative results obtained in France and in Germany in the domain of coloring products.

Let me remind you that the six big German dye companies have formed a consortium since the war, and that this alliance is trying to corner the world market, just as in the case of potash.

In 1920 the profits of the aniline consortium were 250,000,000 marks, permitting the payment of dividends ranging from 15 to 20 per cent. The invested capital amounts to nearly 2,000,000,000, and German manufacturers are growing very anxious because of the protectionist measures taken in the United States. The efforts made in America in the field of dyes show Germany that she cannot seize the world market, and French manufacturers are finding in the example set them by the United States an excellent method of defense against the German monopoly.

I have had occasion to visit the Villers-St. Paul factory, belonging to the Compagnie Nationale des Matières Colorantes et des Produits Chimiques (National Dye and Chemical Company), of which I have already spoken to you. The factory manufactures phthalic acid, rhodamines, safranines, methylene blue, Victoria blue, and hydrosulfite. It has also set up necessary installations for manufacturing intermediate products, such as chloroacetic acid, alizarin and vat dyes, flavazines, tartrazines, etc.

Obviously we are still somewhat lacking as concerns intermediate products, and the option rights granted to the Allies (particularly France) by the Versailles Treaty will play a less and less important part as our production capacity increases.

INDUSTRIAL HYGIENE

The International Bureau of Labor is studying very carefully questions concerning the hygiene of workers, and particularly of workers in the chemical industries.

The methods of investigation used are precisely those developed some time ago in the Bureau of Labor in the United States. Unfortunately, it seems that the conclusions to which these investigations lead have not the approval of all technologists. Attention is drawn particularly to the fact that in the case of white lead the toxicology of that product would not permit demanding its absolute prohibition, contrary to the ideas which have been in vogue for the last ten years.

June 13, 1921

INDUSTRIAL NOTES

A report on lead poisoning in the pottery trades has recently been completed by the United States Public Health Service. The investigation was begun in 1919 and covered 92 potteries situated in New Jersey, Ohio, Pennsylvania, and West Virginia, employing 53 per cent of the total pottery workers in the United States. Risk of lead poisoning was found to differ greatly in the many occupations of the pottery trade, the highest per cent of poisoning being found among the dippers and dippers' helpers. The percentage of poisoning drops as the percentage of lead used in the glaze decreases. The report gives directions for the use of fritted lead glazes, by which great improvement may be brought about.

The following officers of the Manufacturing Chemists' Association have been elected for the ensuing year: Charles L. Reese, *president;* H. H. S. Handy and C. Wilbur Miller, *vice presidents;* S. W. Wilder, *treasurer;* and John L. Tierney, *secretary*. The executive committee consists of Henry Howard, *chairman*, Adolph G. Rosengarten, Lancaster Morgan, C. Wilbur Miller, D. W. Jayne, H. H. Dow, and E. L. Pierce.

Official sanction has been given to the removal of the Chemical Warfare Service activities at Lakehurst, N. J., to Edgewood Arsenal, and the work of removal has been begun. The location at Lakehurst comprises about 16,000 acres. It was established during the war for proving and testing purposes and the building and plants represent an outlay of approximately $1,500,000. The plants, together with machinery, material, and personnel, will be moved to Edgewood. It is believed that the consolidation of the two Chemical Warfare Stations will result in increased economy, efficiency, and harmony for the Service, as it centralizes all the technical activities at Edgewood and will remove much duplication that formerly existed. Edgewood Arsenal will now carry the process of manufacturing the chemical agent from the test tube, through the various stages of development, to filling it into the shell, and finally proving in the field. It is expected that at least 90 per cent of the proof firing can be carried on at Edgewood, where conditions are very favorable.

The John Fritz Medal Board of Award has awarded its gold medal and diploma to Eugene Schneider, head of Le Creusot Steel Works, France, "for achievement in metallurgy of iron and steel; for development of ordnance, especially the 75 mm. gun, and for notable patriotic contribution to the winning of the war." The medal and diploma will be presented to Mr. Schneider in France by a party of American engineers, who will also present the John Fritz gold medal and diploma, which was awarded some time ago, to Sir Robert A. Hadfield "for the invention of manganese steel," so useful in the war and in the industries of peace. The gold medal has previously been awarded to sixteen eminent American and foreign engineers and scientists.

The United States Geological Survey has recently completed a series of experiments on the use of fluorescein by oil men. When mixed with water under certain conditions, fluorescein can be detected easily in a dilution of one part of the dye in 10,000,000,000 parts of water. While most of the experiments have been carried on in regard to surface waters, a firm of engineers has been experimenting with a view to finding out something of the movement of the fluids in the oil sands. In one instance the fluorescein was poured into a well and the hole was shut tight, while the other wells were pumped regularly. It took the solution four days, five hours and a half to appear in a second well more than a mile distant which had practically the same rock pressure.

The New Jersey State Board of Health has served notice on Hemingway & Co. to show cause why an injunction should not be issued forbidding the company to handle phosgene. This action follows the escape of phosgene at the Hemingway plant which resulted in the death of one man and the gassing of many others.

In accordance with the decision of the court on May 4, 1921, permitting the Hercules Powder Company to buy the Aetna Explosives Company, Inc., the Aetna stockholders have sanctioned the sale and the transaction has been closed. By this purchase the Hercules Company will acquire high explosives or dynamite plants near Birmingham, Ala., Emporium, Pa., Sinnamahoning, Pa., Ishpeming, Mich., and Fayville, Ill.; two black blasting powder plants, one at Goes Station, Ohio, and the other near Birmingham, Ala.; a plant for the manufacture of blasting caps and electric blasting caps at Port Ewen, N. Y., and a plant for the manufacture of fulminate of mercury for use in blasting caps, at Prescott, Ontario, Canada. The Hercules Company was originally created by a decree of a federal court in an action brought by the United States against the du Pont Company under the Sherman Act. In sanctioning the purchase of the Aetna, the court stated that actual competition would be undiminished and even probably increased by the transaction, especially in regard to the du Pont Company, the strongest rival.

PERSONAL NOTES

Mr. C. S. Butcher, for the past sixteen years connected with the Semet-Solvay Co., has left that firm to go with the St. Louis Coke and Chemical Co., St. Louis, Mo.

Mr. W. Blair Clark, of the Bureau of Plant Industry, is at present an inspector on the border control work of the Plant Quarantine Law enforcement of the Federal Horticultural Board at El Paso, Texas.

Prof. H. A. Geaque, head of the chemistry department at Simpson College for the past two years, holds a similar position at Lombard College, Galesburg, Ill.

Mr. F. F. Fitzgerald is now chief chemist of the American Can Co., Maywood, Ill., having left the National Canners Association, Washington, D. C.

Dr. T. F. Buehrer has accepted an instructorship in analytical chemistry in the University of Arizona, Tucson, Ariz. He recently received his Ph.D. degree from the University of California.

The death of **Mr. John W. Leitch** of Milnsbridge, England, has recently been reported. Mr. Leitch studied at the Royal College of Science, South Kensington, and graduated B. Sc. at Glasgow University. He then took a post as secretary and chief chemist to a firm of chemical manufacturers at Milnsbridge. Later he established the firm of Messrs. John W. Leitch & Co., at Milnsbridge, and for many years had specialized in the manufacture of coal-tar intermediates and certain dyes.

Mr. Hal T. Beans and **Mr. Thomas B. Freas**, associate professors at Columbia University, New York City, and **Miss Marie Reimer**, associate professor at Barnard College, New York City, have been given the rank of full professors. **Mr. Samuel J. Kiehl**, instructor in chemistry, and **Mr. E. G. Miller, Jr.**, associate in biological chemistry, have been made assistant professors, according to the Trustees' announcement.

Mr. C. L. Bryden, chief engineer for the Kelly Filter Press Co., New York, has associated himself with W. P. Heineken, engineer and manufacturer, of New York City.

According to an agreement recently entered into by the American Foundrymen's Association and the British Association, one original paper will be exchanged between the associations each year. This year the American Association is to present its first paper, and **Mr. George K. Elliott**, chief chemist and metallurgist of the Lunkenheimer Co., Cincinnati, Ohio, and president-elect of the Cincinnati Section of the AMERICAN CHEMICAL SOCIETY, has been selected to write this year's exchange paper, which will deal with the treatment of cast iron in the electric furnace.

Prof. R. Adams Dutcher, has resigned his position in the agricultural biochemistry department of the University of Minnesota, where he was head of the animal nutrition section, to accept the position of chief of the agricultural chemistry department of the Pennsylvania College of Agriculture. At Pennsylvania College, Prof. Dutcher will have a vitamine research laboratory for studies concerning the relation of vitamines to dairy and food products.

Dr. H. P. Talbot, professor of chemistry and Dean of Massachusetts Institute of Technology, received the honorary degree of Doctor of Science from Dartmouth College at the commencement exercises in June 1921.

Mr. Wilfred W. Scott, editor of "Standard Methods of Chemical Analysis," has resigned as research chemist of the General Chemical Co., and has accepted the position of associate professor of chemistry in the Colorado School of Mines.

Mr. John D. Rue, who was previously associated with the Mead pulp and paper interests, has joined the staff of the Forest Products Laboratory at Madison, Wis., as chief of the section of pulp and paper investigations, following the resignation of **Dr. Otto Kress** from that position.

Mr. James L. McClellan has left the Amlac Company of Boston, Mass., to take the position of chief chemist for the National Fibre and Insulation Company of Yorklyn, Del.

Mr. E. A. Richardson has resigned as a member of the glass technology department, National Lamp Works of General Electric Co., Cleveland, Ohio, and has accepted the position of chief chemist for Libbey Glass Mfg. Co., Toledo, Ohio.

Mr. Raymond T. Bohn has been appointed chief chemist of the Nicetown plant of the Midvale Steel and Ordnance Co., succeeding **Dr. G. L. Kelley** who resigned to join the E. G. Budd Co. of Philadelphia and Detroit.

Mr. F. H. Pendleton, formerly chemist with the New England Bureau of Tests of Boston, and more recently research chemist with the Gorton-Pew Fisheries Co., of Gloucester, Mass., has joined the staff of Skinner, Sherman & Esselen, Inc., Boston, Mass.

Mr. W. H. Ransom, formerly Major in the Ordnance Department, U. S. Army, is now connected with the Celluloid Co., of Newark, N. J. Before leaving the service Mr. Ransom was commended in writing by the Chief of Ordnance for "especially meritorious and efficient services."

Mr. L. I. Loghry has resigned from the Mount Joy Magnesia Co., Mount Joy, Pa., and has accepted the position of chief chemist for the Knickerbocker Portland Cement Co., Hudson, N. Y.

Mr. Thomas Blackadder recently severed his connection with the Smethport Extract Co., Inc., of Damascus, Va., where he was located for ten years as chief chemist and works manager, and has come to New York to coöperate with Mr. H. C. Reed of the Reed Laboratories, which specialize in tannin and extract analytical and consulting work.

Mr. Carleton B. Edwards, for the last three years connected with E. I. du Pont de Nemours & Co., at Wilmington, Del., has resigned from that firm, where he was in charge of research in oils, to accept a research position with the Republic Creosoting Co., manufacturers of coal-tar products, at Indianapolis, Ind.

GOVERNMENT PUBLICATIONS

By NELLIE A. PARKINSON, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

FEDERAL TRADE COMMISSION

Summary of Report on Pacific Coast Petroleum Industry. Part I. Production, Ownership, and Profits. 19 pp. Paper, 5 cents. Issued April 7, 1921.

TARIFF COMMISSION

Suggested Reclassification of Chemicals, Oils, and Paints. Report to Congress Suggesting Reclassification of Schedule A and of Related Provisions of Tariff Act of October 3, 1913. 140 pp. Paper, 15 cents. 1921.

Tariff Information Surveys. Revised Edition, 1921.

A-1. On articles in paragraph 1 of tariff act of 1913 and related articles in other paragraphs. **Acids in paragraph 1 and related materials.** 85 pp. Paper, 10 cents.

A-2. On articles in paragraphs 2 and 3 of tariff act of 1913 and related articles in other paragraphs. **Wood chemical industry.** 40 pp. Paper, 5 cents.

A-3. On articles in paragraphs 4–9 of tariff act of 1913 and related articles in other paragraphs. **Balsams, aluminium, and ammonium compounds.** 59 pp. Paper, 5 cents.

A-4. On articles in paragraph 10 of tariff act of 1913 and related articles in other paragraphs. **Barytes, barium chemicals, and lithopone.** 90 pp. Paper, 10 cents.

A-5. On articles in paragraphs 11–17 of tariff act of 1913 and related articles in other paragraphs. **Blacking, cleaning and polishing preparations, and other articles.** 59 pp. Paper, 10 cents.

A-6. On articles in paragraphs 18–26 of tariff act of 1913 and related articles in other paragraphs. **Medicinal, chlorine products, and pyroxylin plastics.** 51 pp. Paper, 5 cents.

A-7. On articles in paragraphs 27–29 of tariff act of 1913 and related articles in other paragraphs. **Crude botanical drug industry, ergot, ethers, and esters.** 81 pp. Paper, 10 cents.

A-8. On articles in paragraphs 30 and 31 of tariff act of 1913 and related articles in other paragraphs. **Tanning materials and natural dyes.** 156 pp. Paper, 15 cents.

A-9. On articles in paragraphs 32–38 of tariff act of 1913. **Formaldehyde, and other articles.** 109 pp. Paper, 10 cents.

A-10. On articles in paragraphs 39–43 of tariff act of 1913 and related articles in other paragraphs. **Buchu leaves, and other articles.** 58 pp. Paper, 10 cents.

A-11. On articles in paragraphs 44 and 45 of tariff act of 1913 and related articles in other paragraphs. **Animal and expressed vegetable oils and fats.** 212 pp. Paper, 20 cents.

A-12. On articles in paragraph 46 of tariff act of 1913 and related articles in other paragraphs. **Essential and distilled oils.** 96 pp. Paper, 10 cents.

A-13. On articles in paragraph 47 of tariff act of 1913. **Opium, cocaine, and their derivatives.** 58 pp. Paper, 5 cents.

A-15. On articles in paragraphs 51–63 of tariff act of 1913 and related articles in other paragraphs. **Pigments, paints, and varnishes.** 210 pp. Paper, 15 cents.

A-16. On articles in paragraph 64 of tariff act of 1913 and related articles in other paragraphs. **Potash industry.** 60 pp. Paper, 5 cents.

A-17. On articles in paragraphs 65 and 66 of tariff act of 1913. **Soaps, salts of tin and bismuth, and rare metals.** 35 pp. Paper, 5 cents.

A-18. On articles in paragraph 67 of tariff act of 1913 and related articles in other paragraphs. **Sodium compounds.** 118 pp. Paper, 10 cents.

PUBLIC HEALTH SERVICE

The United States Public Health Service: Its Evolution and Organization. Public Health Reports, **36,** 1165–76.

GEOLOGICAL SURVEY

Records of Water Levels in Southern California. F. C. EBERT. Prepared in coöperation with the Department of Engineering of the State of California. Water-Supply Paper 468. 156 pp. 1921.

Surface Water Supply of the United States 1918. Part XI. Pacific Slope Basins in California. N. C. GROVER, H. D. MCGLASHAN AND F. F. HENSHAW. Prepared in coöperation with the States of California and Oregon. Water-Supply Paper 481. 314 pp. Paper, 30 cents. 1921.

Geology and Petroleum Resources of Northwestern Kern County, California. W. A. ENGLISH. Bulletin 721. 48 pp. Paper, 10 cents. 1921.

The New Salem Lignite Field, Morton County, North Dakota. E. T. HANCOCK. Bulletin 726-A. Separate from Contributions to Economic Geology, 1921, Part II. 39 pp. Issued May 6, 1921. This bulletin is issued primarily to meet the need of the public for information regarding the fuel resources of the country.

Silver, Copper, Lead, and Zinc in the Central States in 1919 Mines Report. J. P. DUNLOP. Separate from Mineral Resources of the United States, 1919, Part I. 51 pp. Published May 25, 1921. The total value of the mine production of silver, copper, lead, and zinc in the Central States in 1919 was $103,643,361, a decrease of $45,744,705, or about 31 per cent, compared with the value for 1918. The total value of the mine production of these metals for the years 1907 to 1919, inclusive, was $1,246,610,692, of which $511,945,295 was for copper, $441,529,050 for zinc, $288,620,862 for lead, and $4,515,485 for silver. Only in $915, 1916, and 1919 has the value of the recoverable zinc exceeded that of the copper.

Asbestos in 1919. J. S. Diller. Separate from Mineral Resources of the United States, 1919, Part II. 9 pp. Published May 14, 1921. Both the production of asbestos from known deposits and the prospecting for new deposits were carried on vigorously in 1919. The domestic output increased 36 per cent over that of 1918, when conditions were so unfavorable that the quantity produced and sold was only 60 per cent of the output of 1917.

Cadmium in 1920. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1920, Part I. 6 pp. Published May 12, 1921. The report gives the production of cadmium in the United States since the beginning of the industry in 1906, the imports for 1903 and later years, the range of fluctuation in price in 1920, and the yearly average selling price since 1906.

BUREAU OF MINES

The Relative Safety of Brass, Copper, and Steel Gauzes in Miners' Flame Safety Lamps. L. C. Ilsley and A. B. Hooker. Technical Paper 228. 39 pp. Paper, 10 cents. Issued April 1921.

The investigation in the main was conducted along the following lines:

1—A study of European reports on similar research.
2—A selection of critical tests having a bearing on safety.
3—The obtaining of enough material to duplicate such tests.
4—The performance of check tests in accordance with these selections.
5—A report and analysis of the results.

Water-Gas Apparatus and the Use of Central District Coal as Generator Fuel. W. W. Odell. Technical Paper 246. 28 pp. Paper, 5 cents. 1921. This paper was prepared under a coöperative agreement with the Illinois State Geological Survey and the Engineering Experiment Station of the University of Illinois through its Department of Mining Engineering. It presents certain preliminary studies made while considering the possibility of substituting Indiana and Illinois coal for coke in water-gas generator sets.

The Analysis of Sulfur Forms in Coal. A. R. Powell. Technical Paper 254. 21 pp. Paper, 5 cents. 1921. The main purpose of this investigation was to try out further the method of Powell and Parr for the analysis of sulfur forms in coal, to determine its applicability to a variety of coals, and to introduce, if necessary, certain refinements of analysis.

Permeation of Oxygen Breathing Apparatus by Gases and Vapors. A. C. Fieldner, S. H. Katz and S. P. Kinney. Technical Paper 272. 24 pp. Paper, 10 cents. 1921. Tests were made to determine the permeability of the rubber bags of oxygen apparatus to gases and vapors. The breathing bags in vapor of volatile casing-head gasoline showed dangerous penetration. Fabrics made of two rubberized sheets cemented with a glue and glycerol mixture were found completely impermeable; one such fabric had a total thickness one-third that required for rubber.

Reports of Physical Crude Oils from the Producing Fields of the Rocky Mountain District. E. W. Dean, M. B. Cooke and A. D. Bauer. Reports of Investigations. Serial No. 2235. 50 pp. Issued April 1921.

Prevention of Evaporation Losses in Lease Tanks. J. H. Wiggins. Reports of Investigations. Serial No. 2236. 8 pp. Issued April 1921.

Some Factors Affecting Losses of Coal in Mining. G. S. Rice. Reports of Investigations. Serial No. 2237. 6 pp. Issued April 1921.

Coal-Mine Fatalities in the United States 1920 and Coal-Mine Statistics Supplementing Those Published in Bulletin 115. List of Permissible Explosives, Lamps and Motors Tested Prior to January 31, 1921. W. W. Adams. Technical Paper 288. 112 pp. Paper, 15 cents. 1921.

Some Principles Governing the Production of Oil Wells. C. H. Beal and J. O. Lewis. Bulletin 194. Petroleum Technology 61. 58 pp. Paper, 10 cents. 1921. The material for this paper was collected for the most part during the years 1916, 1917, and 1918. The report discusses some of the fundamental factors governing oil production, taking up first the conditions affecting the amount of oil in the oil sand, then those factors that control the rate of production of oil wells, and then discusses several related problems, most of which deal particularly with the effect of the production of one well on that of another.

Gas Masks for Gases Met in Fighting Fires. A. C. Fieldner, S. H. Katz and S. P. Kinney. **With a Chapter on the Effects of Gases on Men and the Treatment of Various Forms of Gas Poisoning.** Yandell Henderson. Technical Paper 248. 71 pp. Paper, 25 cents. The work described in this paper was undertaken to obtain information regarding the use of the Army type of mask for fighting fires and for doing rescue work in mines and the mineral industries. Descriptions of breathing apparatus other than gas masks, descriptions of most of the gases met in the industries, of their physiological effects when inhaled, and of methods of treating persons who have been gassed are included.

The Safety and Health Campaign in the Mining Camps of Utah. C. A. Allen and A. L. Murray. Reports of Investigations. Serial No. 2245. 7 pp. Issued May 1921.

Compressed-Air Blowers in Metal Mines. D. Harrington. Reports of Investigations. Serial No. 2246. 5 pp. Issued May 1921.

The Chloride Volatilization Process. Thomas Varley. Reports of Investigations. Serial No. 2247. 9 pp. Issued May 1921.

The Effect of Crystalline Paraffin Wax upon the Viscosity of Lubricating Oil. E. W. Dean and L. E. Jackson. Reports of Investigations. Serial No. 2249. 3 pp. Issued May 1921. The Bureau of Mines has devised and is using a method for the analysis of crude petroleum which includes the determination of the viscosities of lubricating oil distillates. This method does not provide for the preliminary removal of paraffin wax, and it seemed advisable to determine whether this omission causes any important variation from the results that would be obtained through commercial refinery processing. It was also thought that the tests included in this investigation, though limited in scope, might be of some practical value in indicating the general effect of paraffin content upon one of the most important properties of lubricating oil.

Petroleum Production in South America with Relation to Recent Petroleum Legislation. J. W. Thompson. Reports of Investigations. Serial No. 2250. 4 pp. Issued May 1921. The recent discovery and exploitation of petroleum territory have resulted in the enactment of new petroleum laws in most of the South American republics. These oil fields are admirably located for convenient distribution of petroleum to all the nations using oil as fuel for shipping and industrial concerns. One deterrent to oil production in the republics of South America is the want of inland transportation facilities, but the recent laws of these republics without exception provide for acquiring rights of way for pipe lines and other modes of transportation.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. Reports of Investigations. Serial No. 2252. 30 pp. Issued May 1921.

High-Grade Talc and the California Talc Industry. R. B. Ladoo. Reports of Investigations. Serial No. 2253. 7 pp. Issued May 1921.

BUREAU OF STANDARDS

The Testing of Paper. Circular 107. 37 pp. Paper, 10 cents. 1921. The purpose of this circular is to describe the methods of testing paper used by the paper section of the Bureau of Standards and adopted as a result of testing a large number of samples of various kinds of paper during a period of years. These methods are those that are in common use in paper-testing laboratories. Proposed new methods and special tests are not included in this circular.

Recommended Specification for Flat Interior Lithopone Paint, White and Light Tints. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, January 21, 1921. Circular 111. 8 pp. Paper, 5 cents. 1921. This specification covers ready-mixed lithopone paints, frequently known as flat, washable wall paint, in white and a variety of light tints. Paints under this specification are not intended for outside exposure: they shall dry to dead flat opaque coats that will adhere well to wood, metal, and plaster, stand washing with soap and water, and show no material change in color on exposure to light.

DEPARTMENT OF AGRICULTURE

Effects of Nicotine Sulfate as an Ovicide and Larvicide on the Codling Moth and Three Other Insects. N. E. McIndoo, F. L. Simanton, H. K. Plank and R. J. Fiske. Department Bulletin 938. 19 pp. Paper, 5 cents. Issued May 17, 1921.

The Alcohol Test as a Means of Determining Quality of Milk for Condenseries. A. O. Dahlberg and H. S. Garner. Department Bulletin 944. 13 pp. Issued May 12, 1921. The conclusion is reached that the alcohol test, as ordinarily used, will reject a portion of the unsatisfactory milks, but as a whole it is unreliable and inadequate. There is no direct relation between the coagulation of milk with alcohol and its titratable acidity. The alcohol test shows good possibilities as a practical and reliable test for determining the quality of milk for condenseries making evaporated milk.

Nitrogen and Other Losses during the Ensiling of Corn. R. H. Shaw, P. A. Wright and E. F. Deysher. Department Bulletin 953. 16 pp. Paper, 5 cents. Issued May 14, 1921. This bulletin deals with the losses of nitrogen and other elements in corn silage made under ordinary farm conditions.

Unprotected Electric Lights. A Fire and Explosion Hazard in Dusty Industries. D. J. Price and H. R. Brown. Department Circular 171. 7 pp. Paper, 5 cents. Issued May 1921.

The Influence of Calcium and Phosphorus in the Feed on the Milk Yield of Dairy Cows. E. B. Meigs and T. E. Woodward. Department Bulletin 945. 28 pp. Paper, 5 cents. Issued May 27, 1921.

Methods for Close Automatic Control of Incubating Temperatures in Laboratories. J. T. Bowen. Department Bulletin 951. 16 pp. Issued June 4, 1921.

COMMERCE REPORTS—MAY 1921

South Africa's **mineral** production in 1920 showed an increase of 4,352,799 lbs. over the total for 1919. (Pp. 647–9)

European markets for **paints** and **varnishes** are listed and described. (Pp. 660–71)

Serious experiments as to the utility of **alcohol** as fuel are being carried on in British Guiana. (P. 671)

Prospects for the development of the Austrian **iron** industry are noted. (P. 678)

Great interest is being manifested in the oil discoveries in the MacKenzie River Basin, as well as in the development of the Athabasca River **"Tar Sands."** (P. 681)

The principal raw materials used in the French **chemical** industry are described. (Pp. 684–5)

The more important provisions of the new Brazilian **mining law** are quoted. (P. 686)

Evidence has been brought before the Commonwealth Public Works Committee that the northwest of Western Australia is rich in **gold, copper, tin,** and **coal.** (P. 744)

The discovery of a deposit of **radium-bearing minerals** is reported in the interior of the State of Ceara, Brazil. (P. 746)

Negotiations have been completed whereby the Polish Ministry of Finance leases the **oil distilleries** and government oil fields at Drohobycz to Anglo-Dutch financiers for 20 years. (P. 748)

A native of Burma has secured prospecting licenses covering large areas of **mica** and **gypsum** deposits in Burma and is anxious to communicate with persons in America interested in this product. (P. 818)

The **paper** industry in Latvia is reviewed. (P. 830)

French license requirements for the importation of **petroleum** are cited. (P. 833)

Competent geologists report considerable quantities of **oil** in the Bravos, Iturbide, Camargo, and Ojinaga districts of Chihuahua, Mexico. (P. 876)

The German **potash** industry is encountering difficulties which began with the action of the Federal Potash Council in rejecting the proposition of the potash syndicate for an increase in the domestic price of potash. A number of potash mines have been forced to close down and others are expected to take such action. (Pp. 881–2)

The **copper** market in Japan continues inactive, and there is no immediate prospect of a revival. (P. 886)

The **gold** production of Australia showed a decrease in value in 1920 of £541,924 as compared with the previous year. (P. 896)

The **chemical** and **metal** industry in Latvia is reviewed. (P. 897)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil material by Cuba during the fiscal years ended June 30, 1917, 1918, and 1919. (P. 945)

A recent decree issued in Italy prohibits the use of **white phosphorus** in the manufacture of **matches.** (P. 950)

The **oil seed** industry of South Africa is reviewed. (Pp. 952–7)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil material by Canada during the fiscal years ended March 31, 1918, 1919, and 1920. (P. 970)

The hydrogenation of **oils** in Japan is described. (P. 978)

The **wood-pulp** market in general is exceedingly dull in Sweden (P. 974)

The production of Italian **olive oil** is described. (Pp.983–5).

Regulations for the exportation of Polish **oil** are cited. (pp. 986–7)

The production of **petroleum** in Russia has fallen off seriously, owing to the shortage of labor. (P. 990)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable oil material by Siam during the fiscal years ended March 31, 1918, 1919, and 1920. (P. 992)

Developments are about to begin in a new oil field in Mexico, known as the Iturbide district. (P. 992)

The condition of the **zinc-smelting** industry in Europe is described. (P. 1015)

An article on **oil shale** in Bulgaria is quoted. The article points out the location of deposits of oil shale in Bulgaria and estimates the surface shale at 30,000,000 tons. Bulgaria, according to this article, has the greatest deposit of oil shale yet discovered. (Pp. 1020–1)

A substance resembling brown coal found within 24 miles of Guatemala City and within 15 miles of the railroad has been found to be **ocher.** The supply is said to be almost inexhaustible. (P. 1043)

Dye factories in Lacovia have ceased operations, as a result of a cable from London advising them to stop manufacturing for a while, since there is no demand for the dyes, and prices have consequently fallen. (P. 1074)

The total production of the Alsatian **potash** mines in 1913 was 350,341 tons, corresponding to 56,000 tons of pure potash; in 1919 the production was 464,607 tons, corresponding to 92,006 tons of pure potash; and in 1920 the total reached 1,061,191 tons, corresponding to 199,230 tons of pure potash. (P. 1075)

The production and export of **olive oil** from Malaga is described. (Pp. 1078–9)

The Belgian **chemical** industry is composed of a Fédération des Industries Chimiques de Belgique, which is subdivided into a series of 15 associations. The information for certain associations is missing or incomplete, but the following figures relate to the production of those for which figures could be obtained by the Ministry of Economic Affairs:

Products	1913 Metric tons	1920 Metric tons
Soda, potash, and derivatives:		
Carbonate of soda	31,234	31,000
Caustic soda	3,261	2,418
Chloride of lime	7,444	3,970
Chloride of calcium	6,025	2,850
Potash and derivatives	47,961	40,229
Acids, minerals, and derivatives:		
Sulfuric acid	600,000	400,000
Nitric acid	10,000	7,500
Hydrochloric acid	22,500	27,000
Sulfate of soda	25,000	40,000
Copper ingots	4,000	4,050
Precipitated copper	1,500	800
Superphosphate of lime	465,000	220,000
Wood products for distillation	46,000[1]	21,000[1]
Soap:		
Hard soap	8,700	5,500
Soft soap	17,000	3,800
Powdered soap	2,700	2,270
Matches of wood	490,000,000[2]	382,800,000[2]
Products of coal distillation:		
Alkali	1,500	894
Anhydrous ammonia	40	62
Sulfate of ammonia	22,696	9,048
Benzene, 90 per cent	5,216	4,194
Dissolvent	793	759
Coal tar	37,337	25,872
Naphthalene	5,593	4,702
Creosote oil	8,705	5,543
Tar	47,106	28,304
Light oils	6,277	1,785
Powders and explosives	3,500	2,200

[1] Cubic meters.

[2] Boxes.

The present production figures of purple ore are doubtful, but the pre-war production was 36,000 tons. The present production of artificial silk is about 70 per cent of what it was before the war. (P. 1102)

The production of crude **petroleum** in Rumania for January and February 1921, was 82,977 tons. (P. 1107)

The discovery of **iron** ore is reported in the Czenstochowa District, Poland. (P. 1116)

During the period January-November 1920, the Latvian Factories Inspection Service granted 15 licenses for the organization of **chemical** enterprises. (P. 1119)

The recovery and fuel value of Irish **peat** is described in a report of the British Department of Scientific and Industrial Research on the winning, preparation, and use of peat, particularly in Ireland. (Pp. 1150–1)

The German **oil** mills and **soap** industry have not yet obtained their necessary quota of raw materials. (P. 1152)

The **shale oil** works in northwestern Tasmania have been reopened. (P. 1200)

The Bureau of Foreign and Domestic Commerce has available information concerning the **petroleum** mining laws of Queensland, Victoria, Western Australia, and Tasmania. (P. 1190)

The consumption of **tin** in the Straits Settlements is only about one-third to one-half of the production, and conditions were never more depressing. (Pp. 1212–3)

Considerable deposits of **kaolin, quartz,** and **sand** are being exploited in Upper Austria. The kaolin has been examined and found to meet all of the requirements of the industries for which it can be used. (P. 1214)

Magnesite is being exploited more and more, and new deposits have been discovered in Styria and Tyrol, Austria. (P. 1214)

Considerable quantities of **mica** have been discovered in the Styrian Alps. (P. 1214)

A number of new **oil shale** mines have been opened in Tyrol. (P. 1214)

Reports on the **salt** industry in Cuyutlan, Colima, and in the Yucatan may be obtained from the Bureau of Foreign and Domestic Commerce. (P. 1231)

STATISTICS OF EXPORTS TO THE UNITED STATES

EGYPT—(P. 719)
Hides, skins, and leather
Gum arabic

TAMPICO, MEXICO—(Pp. 727, 869)
Petroleum

MARACAIBO, MEXICO—(P. 753)
Hides, skins
Wax, vegetable
Copaiba

AUCKLAND, NEW ZEALAND—(P. 761)
Copra
Hides
Kauri gum
Tallow

QUEBEC, CANADA—(P. 783)
Acid, sulfuric
Antimony
Asbestos
Gums
Magnesite
Chrome ore
Ferrosilicon
Fertilizer
Hides and skins
Lead concentrates
Leather
Metals
Mica
Oil
Paints
Paper
Rubber
Tin
Pulp wood
Zinc

WELLINGTON, NEW ZEALAND—(Pp.814-5)
Hides
Linseed
Tallow
Whale oil

BRITISH GUIANA—(P. 867)
Bauxite
Chicle
Coconut oil
Copra
Hides
Lime oil
Rosewood essence
Rubber

NAPLES, ITALY—(P. 891)
Crude tartar
Olive oil
Sulfur oil

BELGIUM—(Pp.909-11)
Hides and skins
Crude wax
Ores
Aluminium
Copper, crude
Iron and steel
Lead, crude
Thomas phosphate
Resins
Gold, silver, and platinum

LEGHORN, ITALY—(P. 984)
Olive oil
Sulfur oil
NAPLES, ITALY—(P. 1015)
Crude tartar

GREAT BRITAIN—(P. 1000)
Hides, skins
Lead
Leather

TAIHOKU, TAIWAN—(P. 1019)
Camphor

LIVERPOOL, ENGLAND—(P. 1151)
Ferromanganese
Palm oil

LONDON, ENGLAND—(P. 1165)
Rubber
Tin
Drugs and chemicals
Aluminium
Leather, hides
Linseed oil

CALLAO, PERU—(P. 1177)
Vanadium ore
Hides
Skins
Copper matte

ALSACE-LORRAINE—(P. 1206)
Colors
Chrome
Madder
Glue stock
Gum arabic
Hides
Leather
Potash (chloride, sylvinite)
Potash (muriate)

CANADA—(P. 1220)
Pulp and paper

BOOK REVIEWS

A Dictionary of Chemical Solubilities—Inorganic. By ARTHUR M. COMEY AND DOROTHY A. HAHN. 8 vo. xi + 1141 pp. The Macmillan Co., New York, 1921. Price, $14.00.

The appearance of this valuable book is indeed welcome, the first edition having been long since exhausted. In preparing this edition, which has been brought up to 1916, Dr. Comey has been ably assisted by Miss Hahn.

The plan of the work is the same as that of the first edition, which was modeled largely after the original Storer's "Dictionary of Solubilities," which appeared in 1864.

A compilation of this character is a real necessity to the laboratory and university library. Obviously, the material from which it is drawn is scattered over a very wide range of chemical literature, and the presentation of the material in a unified manner is indeed a valuable contribution. The mere title does not entirely describe all of the contents of the book, inasmuch as a very full list of inorganic compounds is given with the references to the original literature. The book, therefore, also possesses the value of being an almost complete lexicon of inorganic chemistry.

One who has almost worn out a copy of the first edition by constant use cannot but express his appreciation to the authors for the painstaking work of verifying all of the references in the original literature and bringing a vast amount of detail into usable form.

The volume contains the solubility data of the various inorganic substances, be they solids, liquids or gases in water and in many of the nonaqueous liquids. In addition, the important tables of specific gravity and per cent concentration of solutions of acids, alkalies, and salts are given.

The policy of the authors has been to represent the data of the original observers and, instead of making any attempt to criticize, to allow the reader to make his own selections and draw his own deductions.

A future edition of the book might well include compounds of the more common organic acids and their salts, and a few of the more simple organic compounds which are daily in the hands of the inorganic chemist.

The type used is very clear, which is refreshing in a book with so many references. The paper is good, and the mechanical work well done.

VICTOR LENHER

The Technical Examination of Crude Petroleum, Petroleum Products and Natural Gas. By W. A. HAMOR AND F. W. PADGETT. ix + 591 pages. McGraw-Hill Book Co., Inc., New York, 1920. Price, $6.00.

The first half of this book is devoted to the examination of petroleum and its products.

Part II of Chapter I covers the examination and evaluation of crude petroleum. The methods described are very superficial and show an extreme lack of knowledge of modern refining practice. It would be impossible for one to follow the methods therein described and obtain results anywhere near comparable with modern refining practice. The authors state that the Asphalt Base Crude and the Mixed Base Crude can be handled alike. This statement is untrue.

On page 37 the authors state that the maximum quantity of copper oxide required to remove sulfur from the distillates of Ohio Crude was six pounds per barrel, whereas it was nearer twelve pounds.

The second chapter, dealing with the examination of gasoline, is made up largely from abstracts of publications from the Bureau of Mines, reports of the Committee on the Standardization of Petroleum Specifications, and the Bureau of Explosives.

The chapter on the examination of illuminating oil contains a description of a number of obsolete flash cups, as well as those now in use. It contains a description of the burning tests laid down by the Committee on the Standardization of Petroleum Specifications. The authors state that the viscosity of illuminating oil can be taken by the Saybolt thermo-viscosimeter. They give no description of this instrument though it has been in common use for thirty years.

Chapter IV deals with the lubricating oils and greases. On page 91 it is stated that the Engler viscosimeter is specified by certain government departments, whereas, in fact, all government specifications are drawn on the Saybolt viscosimeter. Although this chapter is supposed to be devoted partly to the methods for analysis of grease, no information is given about such methods. On page 118 there are a number of inaccuracies as to its composition.

In discussing bituminous road materials the authors have taken old definitions instead of using those adopted by the American Society for Testing Materials. The greater part of this chapter is abstracted from reports of the Bureau of Public Roads.

Chapter VI deals in a superficial way with fuel and gas oils and in more detail with insulating and cutting oils, petrolatum, and paraffin wax.

Chapter VIII covers the valuation of oil shale.

Chapter IX, on the laboratory method for benzene recovery plant operation, was written by F. W. Sperr, and was published in *Metallurgical & Chemical Engineering* in 1917. In a great many places the plant control is very much simplified from the above description.

Chapter X deals with the examination of natural gas and covers a great deal of the work done by the Bureau of Mines.

The latter part of the book (300 pages) is made up of an appendix containing gravity correction tables, shipping instructions of petroleum products, copies of reports of the American Society for Testing Materials, reports of the Bureau of Standards, and reports of the American Society of Civil Engineers which deal with road construction not even related to petroleum. A great deal of the appendix can be found, word for word, in the first part of the book. It would seem to the reviewer that nearly all the appendix could be eliminated to good advantage, and especially that part which has no relation to petroleum or its products.

G. W. GRAY

A Laboratory Manual for the Detection of Poisons and Powerful Drugs. By WILHELM AUTENRIETH. 5th American edition. Translation of the completely revised 4th German edition, by WILLIAM H. WARREN. xv + 342 pp. P. Blakiston's Son & Co., Philadelphia, 1921. Price, $3.50 net.

This fifth American edition is substantially identical with the fourth American edition [see *J. Am. Chem. Soc.*, **37** (1915), 949]. Only minor changes have been made: corrections of the text, omission of certain tests, corrections of some tests, introduction of a few of the newest tests, and the addition of an index of authors.

This excellent work is particularly useful as a laboratory handbook for students, general and hospital analysts, and pharmacists. A good systematic method of examination for poisons occupies the first 230 pages of the text; the remainder deals with selected special toxicologic analytic methods and concludes with 8 pages of directions for the preparation of special reagents.

One engaged in the preparation of chemical evidence for court trials in poisoning cases would not find in the book much of the information needed for his guidance. Its usefulness in this connection would be greatly enhanced by critical comparisons of the various parallel tests, cautions as to lurking fallacies, and special instructions for blank tests.

G. H. MEEKER

Factory Chemistry. By WM. H. HAWKES. 19 x 13 cm., vii + 59 pp. Longmans, Green and Co., New York, 1921. Price, $1.00.

In the preface the author says: "This text is especially designed for factory men interested in the study of chemistry as it bears on the various operations in factory processes, presenting by simple, clear, and rapid methods, only that part of Chemical Science which will be of daily use and practical value in such departments where a knowledge of Chemistry is of advantage and often indispensable." The chapters are entitled: introduction; valence; definitions and chemical terms; chemical laws; composition, properties, and construction (?) of acids, bases, and salts; classes of salts; hydroxides; chemical equations; classes of equations; mathematics of chemistry; qualitative analysis.

This is a wonderful program, but the performance falls short of the intention. On page 4 the student is told that molecules without a symmetrical arrangement are called colloidal, but of course the author does not mean that. On page 9 the manganate radical MnO_4 is cited as univalent, whereas permanganate is meant. On page 17 Faraday's law is said to be that "when the same quantity of electricity acts upon different electrolytes, the ratio between the quantity of liberated products is the same as between their chemical equivalents." The student is expected to know what quantity of electricity means. One might question the definition, page 16, that an alkali is a base of specially active character. It may be true in a narrow sense to say, page 20, that oxidation is the process of the union of oxygen with other elements, but most of us would speak of oxidizing iron or ferrous chloride with chlorine. On page 23 is the statement that salts with the prefix "per" are derived from supersaturated acids; on page 26 we read that aqua ammonia is strongly alkaline and barium hydroxide weakly alkaline.

One wonders what the student would get out of the following paragraph, page 28, even assuming that it were right:

> To illustrate again take the reaction
>
> $$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O.$$
>
> In the first place the Zn of the Zn hydrate $Zn(OH)_2$ unites with the SO_4 of the H_2SO_4 displacing the H_2, thereby forming the salt $ZnSO_4$: the Zn is bivalent so it will displace the two H's of the acid, and will unite with the SO_4 which is also bivalent, forming a compound which has its two parts each bivalent. The H_2 set free unites with the $(OH)_2$, forming a compound with 4 H's and 2 O's, which unite to form $2H_2O$, or two parts of water.

Part of the paragraph on indicators, page 36, may prove interesting:

> An indicator in chemistry is used to show whether a substance (usually in solution) is alkaline or acid in its properties. Sometimes the amount of acidity or alkalinity is required. Four indicators are in most common use.
>
> *Litmus*—Either as a paper or as a solution. Acid turns this indicator red. Hydrates or bases turn it blue.
>
> *Methyl-orange*—Turns yellow in alkaline solutions and pink in acids, though it is unaffected by CO_2, carbonic acid gas.

The pages which have not been referred to are at least no worse than those which have been considered worthy of special mention. It would have been interesting if the publishers had put in a preface stating why they accepted this book.

WILDER D. BANCROFT

Rubber Manufacture. By H. E. SIMMONS, Professor of Chemistry, Municipal University of Akron, Akron, Ohio. 149 pp. D. Van Nostrand Co., New York, 1921. Price, $4.50.

Professor Simmons deserves general thanks for venturing into print on the subject of rubber manufacture. In few industries has the doctrine of secrecy been more rigidly followed. It is true that plantation crude rubber research has been prosecuted along more open lines, with the result that a considerable body of valuable published work is now available. Research on the chemical constitution of the rubber molecule has also made satisfactory progress. Nevertheless, the systematic study of the technical aspects of rubber manufacturing, including as its two chief branches the study of accelerators and the systematic investigation of compounding ingredients, has hitherto remained locked within the walls of the laboratories of the large companies.

The lack of an authoritative textbook on rubber manufacture is therefore not surprising, and we find that in his book of 149 pages Mr. Simmons has devoted 70 to crude rubber, 26 to a description of various nonrubber compounding ingredients, 23 pages to the chemical and physical testing of vulcanized rubber, and in fact only 12 pages to the factory handling of crude rubber and of the various compounding ingredients. Thus, broadly speaking, the book has really very little to do with "Rubber Manufacture."

The first half of the book describes in lecture style the chief wild and plantation crudes, along with methods of coagulation and preparation. The matter is essentially a summary of material published elsewhere and reduced to lecture form. Chapters are included on elementary colloidal theory, the constitution of rubber (a review of Harries' early work), synthetic caoutchouc, and the chemical and physical testing of crude rubber.

Mr. Simmons next discusses the manufacture of the most important inorganic compounding ingredients. His treatment of this is on the whole quite satisfactory and probably represents as much information as can be derived from the published literature and from casual conversations with "professional" rubber technologists.

Some of the commoner organic accelerators are next described, chiefly from the preparation standpoint. Then follows a very well written chapter on rubber substitutes. The chemical and adsorption theories of vulcanization are set forth in a readable chapter, and the last two chapters are devoted to the chemical and physical testing of manufactured rubber goods.

All of the above matter deals with the materials of the industry before they ever enter the factory portals, and the author confines within two short chapters of 12 pages his discussion of "The Preparation of Crude Rubber for Manufacturing" and "The Principles of Compounding." In the first of these, we find only a brief description of washing and drying machinery, and no reference to such really important technical problems as the sorting of plantation crudes, the classification of incoming shipments of rubber according to curing and tensile properties, the breaking-down of crudes to the proper degree for the varying requirements of mechanical, footwear, and tire work, selection of crudes with respect to cement requirements, blending of wild and plantation rubbers in proper proportions, etc.

"The Principles of Compounding," which are dismissed with 6 pages, might well occupy 600. The matter of this chapter is frequently inaccurate as well as inadequate, as for example the statement that "tensile strength is acquired mainly by the use of zinc oxide and different grades of lampblack," with no reference to sulfur ratios, organic accelerators, resin content of crude rubber, or for that matter other reinforcing pigments such as magnesium carbonate and, above all, carbon black.

In fine, the book will add little to the knowledge of the professional rubber chemist, but will be welcomed by students and graduates just beginning the study of rubber technology. Grammatical obscurities and typographical errors abound (I wonder how Mr. Herbert Wright relishes the description of his work done in 1834, page 26), and it is sincerely to be hoped that the proof in future editions will be more carefully read. The printing and binding are unusually good.

W. B. WIEGAND

A Dictionary of Applied Chemistry, Vol. I. By SIR EDWARD THORPE, C.B., LL.D., F.R.S. 752 pp. Longmans, Green & Co., London, 1921. Price, $20.00.

The revised and enlarged edition of this standard work comes at a time when things chemical are in a stage of active development and readjustment, and therefore is very timely in its appearance.

Vol. I deals with all known substances from Aal to and including calcium compounds, the descriptions given being more comprehensive than in previous editions. The illustrations are numerous and are especially well chosen. Many new compounds are described, and very complete discussions of some of the more important processes are included.

The reader is informed that the entire series has been carefully revised and so much new matter has been included that the completed set will require at least six and possibly seven volumes to do it justice.

The long list of contributors, all of whom stand high in their profession, is a sufficient guarantee that no effort has been spared to make the present and forthcoming volumes a masterpiece of chemical literature. Depicting the relation of chemistry to art and science, it makes the dictionary of inestimable value to anyone who desires to secure genuine information on any subject of chemical nature.

There is no doubt that the book will meet with a hearty reception, and it is felt that the editors should be congratulated upon the results which they have so ably accomplished.

ALLEN ROGERS

Condensed Description of the Manufacture of Beet Sugar. By FRANZ MURKE, PH.D., A.M. 5 × 8½, 175 pp. John Wiley and Sons, Inc., New York, 1921. Price, $2.50 net.

The author states that "this little book was written in 1903-5" ***and on re-reading it he was "impressed by the fact that very few developments had taken place during this time," so that it was easily "brought up to date." Brevity and conciseness in dealing with the main principles, it is hoped, will be welcomed by superintendents, engineers, and foremen in the beet-sugar industry.

The book is divided into twenty chapters. In the main these deal systematically (flow-wise) with the engineering operations involved in the industry. They begin with a chapter upon harvesting the beets and related topics. The last chapter consists of "Tables for Various Calculations," involving formulas, specific gravity, granulation factor, available granulated, temperature correction, and conversion tables.

Ordinary irregularities in operation are discussed and the simple remedies suggested. Practical methods of computation concerning the stations are supplied. Simple evaporator calculation is given, and the so little understood limekiln is dealt with at length.

This book will certainly be a good beginning for any worker in the study of the industry. Its brevity, however, makes it inadequate without amplification in the case of engineering operations. The style is to be complimented for its brevity, though it is discursive rather than clearly summarized as to important operating points to be borne in mind. Classification of the chapters into subtopics would have rendered the importance of some matters more evident. The chapter on limekilns, for instance, would have profited by such an arrangement. A few curves would also have helped at various points. For instance, in the chapter on storing, a curve showing the relation of the rate of storing and the rate of slicing would give a means of determining the tons of beets on hand, an important matter.

It might have been advisable to assume a definite capacity for a factory and to calculate the products of each station on the same assumption and not to vary the calculation basis, by assuming 1000 tons of beets per 24 hours on page 127 and 1000 kg. on page 52.

There is no form of calculation for tonnage of "thin juice," "thick juice," or "water evaporated." A little more of definitions would have been clarifying. No indication is given of the labor required at the various stations. The author's logical arrangement renders, in part, a flow sheet unnecessary, though it would have helped a beginner. The absence of an index is noticeable.

Though the book purports to be concerned with American practice, such abbreviations as "70 HL" would probably be more easily understood by German workers as meaning "hecta liters" than by Americans. Methods and steps of calculations could be made more clear.

The formation of glucose is well explained, as is also its effect in the vacuum pan. The author shows thorough knowledge of the subject, such as can be acquired only by years of experience. His points of emphasis are those of great importance to the industry.

JAMES R. WITHROW

Labor's Crisis. By Sigmund Mendelsohn. xii + 171 pp. Macmillan Co., New York, 1920. Price, $1.50.

This little book presents a clear picture of the status of labor and capital. It is an unusually thorough and unbiased analysis of the world-wide change in the relative position of capital and labor that springs from the war and the Russian Revolution. "The labor problem is more acute than ever, but it concerns the welfare of society more than of labor," says Mendelsohn. He points out that labor is not paramount. There are four factors of production: capital, labor, intellect, and mechanical power. The use of power has been made possible by intellect, and power is a greater factor in modern industry than manual labor.

"The European upheaval is not only changing the map of the world; it is not only revolutionizing political institutions by basing them on democratic, or even on socialistic principles; but it is also creating a new social era, in which the order of society is being reversed, and those who were at the bottom are becoming the ruling power." Intellectual and scientific workers are in danger of being sacrificed and submerged in the turmoil.

Mendelsohn, too, emphasizes the fact that much of labor unrest springs from transplanting labor from the land "into congested industrial centers, where ideals do not thrive, individuality and ambition are weakened, and the worker is reduced to a integral part of the mechanism which he is operating."

He calls attention to the probability that capital in the future will not have the unhampered powers and opportunities it enjoyed in the past. "Though a closer bond between capital and labor will involve shrinkage in profit from capital, and as a consequence may weaken the stimulus for industrial enterprise, this will to some extent be offset by offering capital greater stability and security.

"The relationship of capital and labor, while it concerns more directly the two parties, involves a third interest, the public, which is distinctly and vitally interested. Labor unrest is a symptom not of disease and decline, but of life and vitality. It is the expression of aspirations, and, threatening and disturbing as the movement may seem, it will eventually lead to a more perfect social order."

The book discusses housing, women in industry, the eight-hour day, and the forty-four-hour week. It points to the humanitarian merits of intermediate sized-factories and medium cities, which permit expression of individuality that is suppressed or lost in huge plants and cities.

The chemist or engineer who studies the literature of labor becomes convinced that it pays to advertise. Organized labor is honored with many books and daily front-page attention. But the intellectual workers, whether clerical people, teachers, university professors, or technical men, receive scant notice, because they give no publicity to their own social worth and economic value. And they make little hue and cry about the straits in which they are caught by the declining value of the dollar. Labor, capital, intellect, these three have conquered the forces of nature, through modern industry. Yet labor keeps its two helpmates on the defensive by its insistence and publicity.

H. W. Jordan

Ammonia and the Nitrides. By Edward B. Maxted, Ph.D., B.Sc., F.C.S. viii + 116 pp. P. Blakiston's Son & Co., Philadelphia, 1921. (*Printed in Great Britain.*) Price, $2.00.

Dr. Maxted has gathered in this little book much information that is of general interest as well as of particular importance to those interested in the problem of nitrogen fixation. The author is especially fitted to take up with utmost thoroughness the entire subject he has undertaken and to correlate much of the information at present available from the literature on the subject. His own researches in this field have been sufficiently extended to make important any viewpoints he cares to bring forth. He has, however, preferred not to make the present small volume of such broad scope as the subject would permit and has touched upon only the general principles and the most important data.

The book is written in a very readable manner, and the material is most logically arranged. There have been avoided those details and argumentative discussions which so often lead to confusion rather than enlightenment of a majority of readers. The information given is easily accessible, and to the point.

The book is divided into seven chapters, the first two of which refer to the direct synthesis of ammonia from its elements, taking up the ammonia equilibrium and its determination, as well as touching upon experimental work on the catalysis of the ammonia reaction. The next four chapters take up in the order of the periodic system the nitrides of the various elements, giving for each the mode of preparation and the characteristic properties. The last chapter discusses that very interesting subject, activated nitrogen.

R. S. Tour

Gasoline and Other Motor Fuels. By Carleton Ellis and Joseph V. Meigs. 709 pp. D. Van Nostrand Co., New York, 1921. Price, $10.00 net.

The preface of this book begins with the statement: "The field of motor fuel has become so enormous that a special treatise on this subject seems to be warranted." The authors can hardly claim the distinction of being the first or sole discoverers of this fact, but this will not lessen the credit due them for a work that meets a long-felt need in the field of petroleum technology. Examination of the volume confirms the claim that it constitutes a substantially complete survey, and as such it will be welcomed by workers who have to collect information and reject misinformation from a scattered and frequently inaccessible literature.

The book includes twenty-seven chapters, a preface, an introduction, and an appendix. The preface outlines admirably the scope of the work, and answers, before they are definitely formulated, certain questions that are likely to come to the mind of the reader. The introduction outlines what is frequently referred to as "the motor fuel problem" and indicates certain developments that are desirable in the refinins industry.

The first four chapters deal with the general characteristics of motor fuels, testing and analytical methods, and conventional refinery procedure for the production of finished gasoline from crude petroleum. Chapters 5 to 22, inclusive, deal with what are usually classed as cracking processes. These processes are classified in several groups and are carefully reviewed, principally through information obtainable in the patent literature. Chapter 23 deals with processes for the extraction of gasoline from natural gas. Chapters 24 and 25 deal with the use and manufacture of benzene and alcohol, respectively, which are the two motor fuels generally regarded as the most promising substitutes for petroleum derived gasoline. A brief discussion of shale as a source of motor fuel is given in Chapter 26, and the pyrogenic treatment of asphalts is dealt with in Chapter 27.

The appendix includes statistical and general information regarding the refining of crude petroleum, the production and utilization of gasoline from natural gas, and the coking industry. There are several useful tables showing chemical and physical properties of hydrocarbons occurring in various types of motor fuel.

The book is one that probably will be found easy to criticize, but the reviewer ventures to predict that the men who are qualified to suggest additions and corrections are certain to be among those who use it most frequently.

E. W. Dean

NEW PUBLICATIONS

Ceramics, a Manual for Chemists, Engineers and Manufacturers, Including a Collection of Tables and Problems for Laboratory and Plant Use, with a Dictionary of Useful Minerals. Andrew Malinovzsky. 274 pp. Illustrated. Price, $3.00. D. Van Nostrand Co., New York.

Chemical Reactions and Their Equations. Ingo W. D. Hackh. 138 pp. Price, $1.75 net. P. Blakiston's Son & Co., Philadelphia.

Coke-Oven and By-Product Works Chemistry. Thos. Biddulph-Smith. 180 pp. Illustrated. J. B. Lippincott Co., Philadelphia.

Coal-Tar: La Technique Moderne de l'Industrie des Goudrons de Houille. C. Berthelot. 104 pp. 53 fig. Price, 15 fr. Dunod, Paris.

Engineering Instruments and Meters. Edgar A. Griffiths. 360 pp. Illustrated. Price, $7.50. D. Van Nostrand Co., New York.

Ingots and Ingot Moulds. Arthur W. Brearley and Harry Brearley. 218 pp. Illustrated. Price, $5.50 net. Longmans, Green & Co., New York.

Nitrate: The Recovery of Nitrate from Chilean Caliche. A. W. Allen. 50 pp. Chas Griffin & Co , Ltd., London.

Organic Analysis: Manual Pratique d'Analyse Organique. Frank E. Weston. 2d French edition. 128 pp. Illustrated. Price 12 fr. Dunod, Paris.

Petroleum: Le Petrole, son Utilisation comme Combustible. A. Masméjean and E. Berehare. 232 pp. Illustrated. Price, 40 fr. Dunod, Paris.

Practical Leather Chemistry, a Hand Book of Laboratory Notes and Methods for the Use of Students and Works' Chemists. Arthur Harvey. 200 pp. Illustrated. Price, $3.75. D. Van Nostrand Co., New York.

Pulp and Paper: The Manufacture of Pulp and Paper. Volume II. Mechanics and Hydraulics, Elements of Electricity, Elements of Chemistry. J. J. Clark and T. L. Crossley. 525 pp. Illustrated. Price, $5.00 McGraw-Hill Book Co., Inc., New York.

Reports of the Progress of Applied Chemistry. Vol. V, 1920. Society of Chemical Industry, London. 626 pp. Price, 8s. 3d. to members, 15s. to non-members.

Silica and the Silicates. J. A. Audley. Industrial Chemistry Series. 374 pp. Price, 15s. net. Baillière, Tindall & Cox, London

Soap: La Chimie du Savonnier et du Commerce de Corps Gras. R. Ehrsam. 380 pp. Illustrated. Price, 48 fr. Dunod, Paris.

Tables of Physical and Chemical Constants and Some Mathematical Functions. G. W. C. Kaye and T. H. Laby. 4th edition. 161 pp. Price, $4.00. Longmans, Green & Co., New York.

Textile Soaps and Oils: A Handbook on the Preparation, Properties, and Analysis of the Soaps and Oils Used in Textile Manufacturing, Dyeing and Printing. George H. Hurst. 3d revised edition, by W. H. Simmons. 200 pp. 12 illustrations. Price, 11s. Scott, Greenwood & Son, London.

RECENT JOURNAL ARTICLES

Absorption: Contributions to the Stoichiometry of Adsorption. I. Adsorption of Cations of the Alkalies and Alkaline Earths. Sven Odén and Hugo Andersson. *Journal of Physical Chemistry*, Vol. **25** (1921), No. 4, pp. 311–331.

Air Trouble in Gasoline Recovery. O. J. Sieplein. *The Gas Age*, Vol. **47** (1921), No. 9, pp. 364–65.

Alcohol: La Determinazione Ebulliometrica dell' Alcool nei Vini. Ugo Pratolongo. *Giornale di Chimica Industriale ed Applicata*, Vol. **3** (1921), No. 4, pp. 143–47.

Alloys: La Theorie des Alliages Metalliques et ses Principales Consequences Industrielles. Léon Guillet. *Chimie et Industrie*, Vol. **5** (1921), No. 4, pp. 371–83.

Aluminium: Iron-Pot Melting Practice for Aluminium Alloys. Robert J. Anderson. *The Metal Industry*, Vol. **19** (1921), No. 5, pp. 189–90; No. 6, pp. 246–47.

Antimony Sulfuret, Its Manufacture and Use. D. A. Shirk. *The Rubber Age*, Vol. **9** (1921), No. 3, pp. 87–90.

Blast Furnace Gases: Adapting Electrical Cleaning to Blast Furnace Gases. N. H. Gellert. *American Gas Journal*, Vol. **114** (1921), No. 22 (Whole No. 3299), pp. 465–67, 473–76.

Butter: The Detection of Adulteration in Butter by Means of the Melting Point of the Insoluble Volatile Acids. George Van B. Gilmour. *The Analyst*, Vol. **46** (1921), No. 542, pp. 183–87.

Butter: Investigations on the Rancidity of Butter and Margarine Fats. W. N. Stokoe. *Journal of the Society of Chemical Industry*, Vol. **40** (1921), No. 8, pp. 75*t*–81*t*.

Chemical Warfare: The Case for Chemical Warfare. Sir William J. Pope. *The Chemical Age* (London), Vol. **4** (1921), No. 99, pp. 526–28.

Coal: L'Evolution dans la Recuperation et le Traitement des Sous-Products de la Carbonisation de la Houille. Ch. Berthelot. *Chimie et Industrie*, Vol. **5** (1921), No. 4, pp. 384–97.

Colloidal Clay and the Hydrolysis of Oils and Fats—I. Frank E. Weston *The Chemical Age* (London), Vol. **4** (1921), No. 102, pp. 604–05.

Combustion: Determination of Excess Air from Flue Gas Analysis. R Brown. *Combustion*, Vol. **4** (1921), No. 6, pp. 24–25.

Costing for Chemical Manufacturers. Alfred E. Vago. *The Chemical Trade Journal and Chemical Engineer*, Vol. **68** (1921), No. 1773, pp. 621–22.

Cyanide Notes. Algernon Del Mar. *Mining and Scientific Press*, Vol. **122** (1921), No. 24, pp. 810–12.

Diseases of Occupation. Stephen Miall. *Journal of the Society of Chemical Industry*, Vol. **40** (1921), No. 8, pp. 140*r*–43*r*.

Dyes: Properties and Application of the Rhodamines. John MacGregor. *Color Trade Journal*, Vol. **8** (1921), No. 6, pp. 229–33.

Froth Flotation as Applied to the Washing of Industrial Coal. Ernest Bury, Walter Broadbridge and Alfred Hutchinson. *The Canadian Mining Journal*, Vol. **42** (1921), No. 20, pp. 405–10.

Fuel Economy of a Drop Forge Plant. N. A. Craigue and C. H. L. Thompson. *The Iron Age*, Vol. **107** (1921), No. 23, pp. 1521–25.

Fuel Oil and Its Combustion. Robert June. *Combustion*, Vol. **4** (1921), No. 6, pp. 26–29.

Glassware: Progress in the Manufacture of English Chemical and Scientific Glassware. J. H. Davidson. *Canadian Chemistry and Metallurgy*, Vol. **5** (1921), No. 6, pp. 165–66.

Glucosan. Ame Pictet and Pierre Castan. *Paper*, Vol. **28** (1921), No. 12, pp. 20–21. Translated from *Helvetica Chimica Acta*.

Hydrolysis of Fats by Reagents Made from Cymene. Ralph H. McKee and Leland J. Lewis. *Chemical and Metallurgical Engineering*, Vol. **24** (1921), No. 22, pp. 969–75.

Internal Combustion Engine: Heat Value of Gases. Mark Meredith. *American Gas Journal*, Vol. **114** (1921), No. 20 (Whole No. 3297), pp. 425–26.

Leather: Action du Carbonate de Soude sur les Solutions d' Alum de Chrome. Louis Meunier. *Journal of the Society of Leather Trades' Chemists*, Vol. **5** (1921), No. 4, pp. 103–11.

Lenses: Processes in the Manufacture of Lenses. Donald E. Sharp. *The Glass Industry*, Vol. **2** (1921), No. 6, pp. 133–37.

Lime: Opportunity of Technical Men in the Lime Industry. Harvey S. Owen. *Rock Products*, Vol. **24** (1921), No. 12, pp. 33–34.

Linseed Oil: L'Huile de Lin et ses Applications. H. de la Condamine. *L'Industrie Chimique*, Vol. **8** (1921), No. 38, pp. 174–77.

Metal Plating: Gold Plating. W. G. Knox. *The Metal Industry*, Vol. **19** (1921), No. 6, pp. 236–39.

Metallurgy: Esame Comparativo dei Metodi Analitici Applicati alle Leghe Metalliche. F. Graziani and L. Losana. *Giornale di Chimica Industriale ed Applicata*, Vol. **3** (1921), No. 4, pp. 148–52.

Metallurgy: La Metallurgie Electrothermique et Electrolytique du Ferro-Nickel. Jean Escard. *L'Industrie Chimique*, Vol. **8** (1921), No. 38, pp. 168–72.

Newsprint Industry: The Role of the Chemical Engineer in the Newsprint Industry. R. W. McKenzie. *Paper*, Vol. **28** (1921), No. 8, pp. 15–16; No. 9, pp. 20–21; No. 10, pp. 19–21; No. 11, pp. 24–25, 41.

Nickel Oxide in Glazes. J. D. Whitmer. *Journal of the American Ceramic Society*, Vol. **4** (1921), No. 5, pp. 357–65.

Nickel: The Use of Fluorides in Solutions for Nickel Deposition. William Blum. *Brass World*, Vol. **17** (1921), No. 5, pp. 121–27.

Oils, Fats, Waxes and Resins Used in the Rubber Industry. Frederic Dannerth. *India Rubber World*, Vol. **64** (1921), No. 2, pp. 563–66.

Paint: The Chemistry of Paints and Varnishes. R. S. Morrell. *The Chemical Age* (London), Vol. **4** (1921), No. 98, pp. 497–99.

Paint: Preservation of Chemical Works Plant and Structures: Protective Uses of Paint, Varnish, Tar, etc. G. B. Jones. *The Chemical Age* (London), Vol. **4** (1921), No. 98, pp. 494–95.

Photography: A Propos de l'Action du Persulfate d'Ammoniaque sur l'Argent des Phototypes et des Anomalies Observees dans l'Emploi de ses Solutions. A. and L. Lumière and A. Seyewetz. *Bulletin de la Société Francaise de Photographie*, Vol. **8** (1921), No. 2, pp. 45–50.

Portland Cement: A Critical Review of Wet Process for Manufacture of Portland Cement. Richard K. Meade. *Concrete*, Vol. **18** (1921), No. 5, pp. 135–43

Post-Graduate Training in Industrial Chemistry. Francis H. Carr. *Journal of the Society of Chemical Industry*, Vol. **40** (1921), No. 9, pp. 161*r*–64*r*.

Rubber: The Relative Accelerating Action of Different Compounds of Lead in the Vulcanizing of Rubber. J. M. Grove *India Rubber World*, Vol. **64** (1921), No. 3, pp. 663–64.

Rubber: The Relative Thermal Conductivity of Some Rubber Compounds. A. A. Somerville. *The Rubber Age*, Vol. **9** (1921), No. 4, p. 131.

Steel: Considerations on the Welding of Steel. H. Brearley. *The Blast. Furnace and Steel Plant*, Vol. **9** (1921), No. 6, pp. 361–67.

Steel: Manufacture and Properties of Molybdenum Steels. Arthur H. Hunter. *The Iron Age*, Vol. **107** (1921), No. 22, pp. 1469, 1511–12.

Steel: Modern Steel Works Power Plant. W. N. Flannigan. *The Blast Furnace and Steel Plant*, Vol. **9** (1921), No. 6, pp. 350–56.

Textiles: Carbonizing Raw Stock and Piece Goods. Frederick Albert Hayes. *Textile World*, Vol. **59** (1921), No. 24, pp. 27–29.

MARKET REPORT—JUNE, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		June 1	June 15
Acid, Boric, cryst., bbls	lb.	.14	.14
Hydrochloric, com'l, 20°	lb.	.01½	.01½
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07¼	.07¼
Phosphoric, 50% tech	lb.	.18	.18
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	18.00	18.00
Oleum 20%	ton	23.00	23.00
Alum, ammonia, lump	lb.	.04	.03¾
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	.09	.09
Ammonium Chloride, gran	lb.	.06¾	.06¾
Ammonia Water, carboys, 26°	lb.	.09¾	.09¾
Arsenic, white	lb.	.07	.06½
Barium Chloride	ton	65.00	60.00
Nitrate	lb.	.10	.09
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	2.75	2.75
Borax, cryst., bbls	lb.	.06½	.06
Bromine, pure	lb.	.27	.27
Calcium Chloride, fused	ton	28.75	28.75
Chalk, precipitated, light	lb.	.04	.04
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.25	5.62½
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.75	3.75
Lead Acetate, white crystals	lb.	.13	.13
Nitrate	lb.	.15	.15
Red American	100 lbs.	.11¼	.11¼
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	1.40	1.40
Magnesium Carbonate, tech	lb.	.10½	.10½
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	47.00	46.00
Phosphorus, yellow	lb.	.30	.30
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.11½	.11½
Bromide, cryst	lb.	.16	.16
Carbonate, calc., 80–85%	lb.	.05	.05
Chlorate, cryst	lb.	.09	.09
Hydroxide, 88–92%	lb.	.05	.05
Iodide, bulk	lb.	2.60	2.65
Nitrate	lb.	.10	.10
Permanganate, U. S. P.	lb.	.27	.27
Salt Cake, bulk	ton	35.00	35.00
Silver Nitrate	oz.	.41	.40
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.00	2.25
Caustic, 76%	100 lbs.	4.00	4.25
Sodium Acetate	lb.	.06	.06
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.08¼	.08¼
Chlorate	lb.	.07½	.07½
Cyanide	lb.	.20	.20
Fluoride, technical	lb.	.12	.12
Hyposulfite, bbls	100 lbs.	4.00	4.00
Nitrate, 95%	100 lbs.	2.70	2.70
Silicate, 40°	lb.	.01½	.01½
Sulfide	lb.	.07	.07
Bisulfite, powdered	lb.	.06	.06
Strontium Nitrate	lb.	.12½	.12½
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride	lb.	.18	.18
Oxide	lb.	.40	.40
Zinc Chloride, U. S. P.	lb.	.40	.40
Oxide, bbls	lb.	.09	.09

ORGANIC CHEMICALS

		June 1	June 15
Acetanilide	lb.	.27	.27
Acid, Acetic, 28 p. c.	100 lbs.	2.75	2.75
Glacial	lb.	.11	.11
Acetylsalicylic	lb.	.58	.58
Benzoic, U. S. P., ex-toluene	lb.	.65	.65
Carbolic, cryst., U. S. P., drs	lb.	.10	.10
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	.44	.45
Acid (*Concluded*)			
Oxalic, cryst. bbls	lb.	.16½	.20
Pyrogallic, resublimed	lb.	1.85	1.85
Salicylic, bulk, U. S. P.	lb.	.21	.20
Tartaric, crystals, U. S. P.	lb.	.30	.29
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.13½	.13½
Alcohol, denatured, complete	gal.	.37	.37
Ethyl, 190 proof	gal.	4.75	4.75
Amyl Acetate	gal.	3.05	3.05
Camphor, Jap. refined	lb.	.68	.73
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.12	.12
Chloroform, U. S. P.	lb.	.43	.43
Creosote, U. S. P.	lb.	.45	43
Cresol, U. S. P.	lb.	.18	.18
Dextrin, corn	100 lbs.	3.15	3.15
Imported Potato	lb.	.07½	.07½
Ether, U. S. P., conc., 100 lbs.	lb.	.18	.18
Formaldehyde	lb.	.14	.14
Glycerol, dynamite, drums	lb.	.14	.13
Methanol, pure, bbls	gal.	1.25	1.25
Pyridine	gal.	2.75	2.75
Starch, corn	100 lbs.	2.33	2.33
Potato, Jap	lb.	.05	.05
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		June 1	June 15
Beeswax, pure, white	lb.	.45	.45
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.08½	.08½
Ceresin, yellow	lb.	.12½	12½
Corn Oil, crude, tanks, mills	lb.	.05½	.05½
Cottonseed Oil, crude, f. o. b. mill.	lb.	.05½	.05¾
Linseed Oil, raw (car lots)	gal.	.75	.76
Menhaden Oil, crude (southern)	gal.	.30	.30
Neat's-foot Oil, 20°	gal.	1.00	1.00
Paraffin, 128–130 m. p., ref	lb.	.07	.07
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.35	5.40
Rosin Oil, first run	gal.	.40	.40
Shellac, T. N.	lb.	.70	.70
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.75	.75
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.65	.60

METALS

		June 1	June 15
Aluminium, No. 1, ingots	lb.	.23	.23
Antimony, ordinary	100 lbs.	5.12½	5.12½
Bismuth	lb.	1.50	1.50
Copper, electrolytic	lb.	.12¾	.12¾
Lake	lb.	.13	.13
Lead, N. Y.	lb.	.04¼	.04¼
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	65.00	65.00
Quicksilver, flask	75 lbs. ea.	47.00	46.00
Silver	oz.	.60	.60
Tin	lb.	.29	.29
Tungsten Wolframite	per unit.	3.25	3.25
Zinc, N. Y.	100 lbs.	4.75	4.75

FERTILIZER MATERIALS

		June 1	June 15
Ammonium Sulfate, export	100 lbs.	2.50	2.50
Blood, dried, f. o. b. N. Y.	unit	3.50	3.50
Bone, 3 and 50, ground, raw	ton	45.00	45.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	3.50 & .10	3.50 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	11.00	11.00
Tennessee, 78–80%	ton	15.00	15.00
Potassium Muriate, 80%	unit	1.00	.90
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	2.75 & .10	2.75 & .10

COAL-TAR CHEMICALS

Crudes

		June 1	June 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U. S. P.	lb.	.18	.18
Cresylic Acid, 97–99%	gal.	.90	.90
Naphthalene, flake	lb.	.08	.08
Phenol, drums	lb.	.10	.10
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.60	.60

Intermediates

		June 1	June 15
Acids.			
Anthranilic	lb.	1.80	1.80
B	lb.	2.25	2.25
Benzoic tech	lb.	.60	.60
Broenner's	lb.	1.75	1.75
Cleve's	lb.	1.30	1.30
Gamma	lb.	3.25	3.25
H	lb.	1 10	1.10
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.75	2.75
Naphthionic, crude	lb.	.75	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.30	.30
Tobias'	lb.	2.25	2.25
Aminoazobenzene	lb.	1.25	1.25
Aniline Oil	lb.	.19	19
For Red	lb.	.42	.42
Aniline Salt	lb.	28	.28
Anthraquinone	lb.	1.75	1.75
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.50	1.50
Benzidine (Base)	lb.	1.00	.90
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	6.00	6.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb	.45	.45
Dinitrobenzene	lb.	.25	.25
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.60	.60
G Salt	lb.	.80	.80
Hydroquinol	lb.	1.55	1 35
Metol (Rhodol)	lb.	6.75	6.75
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.38	.38
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.38	.38
m-Nitroaniline	lb.	.90	.90
p-Nitroaniline	lb.	.85	.85
Nitrobenzene, crude	lb.	.12$^{1}/_{2}$	.12$^{1}/_{2}$
Rectified (Oil Mirbane)	lb.	.13$^{3}/_{4}$	.13$^{3}/_{4}$
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.90	.90
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.75	1.75
Phthalic Anhydride	lb.	.55	.55
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.75	.75
Resorcinol, tech	lb.	1.75	1.75
U. S. P.	lb.	2.25	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.60	.60
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.27	.27
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		June 1	June 15
Black	lb.	1.00	1.00
Blue	lb.	1.50	1.50

Acid Colors (*Concluded*)

		June 1	June 15
Fuchsin	lb.	2.50	2.50
Orange III	lb.	.60	.60
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4 00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.85	.85

Direct Colors

		June 1	June 15
Black	lb.	.90	.90
Blue 2B	lb.	.70	.70
Brown R	lb.	1.65	1.65
Fast Red	lb.	2.35	2.35
Yellow	lb.	2.00	2.00
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		June 1	June 15
Black	lb.	.70	.70
Blue	lb.	.80	.80
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		June 1	June 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		June 1	June 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	1.00	1.00
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	2.80	2.80

Basic Colors

		June 1	June 15
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.80	80
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	4.50	4.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	2.75	2.75
Methylene Blue, tech	lb.	2.75	2.75
Methyl Violet 3 B	lb.	2.75	2.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	16.00	16.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of

INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society

Editor: CHAS. H. HERTY

Assistant Editor: LOIS W. WOODFORD

Advisory Board: H. E. BARNARD J. W. BECKMAN A. D. LITTLE A. V. H. MORY
CHAS. L. REESE GEO. D. ROSENGARTEN T. B. WAGNER

EDITORIAL OFFICES:
One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613–0614

Cable Address: JIECHEM

ADVERTISING DEPARTMENT:
170 Metropolitan Tower
New York City
TELEPHONE: Gramercy 2145

Volume 13 AUGUST 1, 1921 No. 8

CONTENTS

EDITORIALS:

A Time for Gathering 670
Have You Done Your Share 670
Restoration in Poland 671

ORIGINAL PAPERS:

The Water Resistance of Treated Canvas during Continuous Exposure to Weather. F. P. Veitch and T. D. Jarrell 672
The Effect of Certain Fire-Proofing Solutions on Cotton Fabric. R. L. Sibley 676
The Use of Nitroglycerin Spent Acid as Charging Acid for Nitric Acid Stills. S. G. Norton 677
The Thermal Decomposition of Oil Shales. II—Determination of the Heat of Reaction Involved in Their Thermal Decomposition. Ralph H. McKee and E. E. Lyder 678
The Rare Sugars: Their Purity and Tests. Carl Pfanstiehl and Robert S. Black 685
The Standardization of Rare Sugars. Howard T. Graber 687
Soy-Bean Oil: Factors Which Influence Its Production and Composition. Carl R. Fellers 689
The Alkalinity of Searles Lake Brine. Roger C. Wells. 691
Action of Lime on Greensand. R. Norris Shreve 693
The Determination of Small Quantities of Zinc. M. Bodansky 696
A Simple Method for the Determination of Vanadium in Ores and Metallurgical Products. R. B. Schaal 698
The Gold Number of Commercial Gelatins. Felix A. Elliott and S. E. Sheppard 699

LABORATORY AND PLANT:

Distillation Apparatus. Paul Gross and Alexander H. Wright 701
The Consistency of Starch and Dextrin Pastes. Winslow H. Herschel and Carl Bergquist 703
The Modulus of Hardness of Vulcanized Rubber. H. P. Gurney 707
The Examination of Sugar Crystals by Projection. George P. Meade 712
Modified Laboratory Apparatus. C. C. Kiplinger 713

ADDRESSES AND CONTRIBUTED ARTICLES:

Incendiaries in Modern Warfare. Arthur B. Ray 714
Some New Features in Limekiln Construction. Richard K. Meade 722
Standardization and Research. S. W. Stratton 727
The Measurement of Color. C. E. K. Mees 729

SOCIAL INDUSTRIAL RELATIONS:

Out-of-Door Education for the Chemist. H. W. Jordan 731

SCIENTIFIC SOCIETIES:

Chemistry's Greatest Rally; The Chemical Exposition; Reagent Chemicals. I—Proposed Specification for Sulfuric, Nitric, and Hydrochloric Acids, and for Ammonium Hydroxide; Membership Directory of the Society; Calendar of Meetings 733

THE SECOND INTERNATIONAL CHEMICAL CONFERENCE 737

MISCELLANEOUS:

American Ceramic Society Meeting at St. Louis, Mo., in 1922 684
Platinum Theft 697
Symposium on Chemistry in Coking and Gas Industries; New York Meeting, American Chemical Society 706
Society of Chemical Industry 732
Chemical Control Committee, National Fertilizer Association 738

WASHINGTON LETTER 739
LONDON LETTER 740
PERSONAL NOTES 741
INDUSTRIAL NOTES 742
GOVERNMENT PUBLICATIONS 742
BOOK REVIEWS 745
NEW PUBLICATIONS 746
MARKET REPORT 747

Subscription to non-members, $7.50; single copy, 75 cents, to members 60 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.

EDITORIALS

A Time for Gathering

The period September 6 to 17, 1921, looms large in its potentialities for chemistry in America. Chemists of England, Canada and the United States will then gather to make fast the ties that naturally bind them, to discuss matters of scientific importance, to determine policies which should prove of lasting benefit in future development and to speak in united voices to our several peoples about those subjects on which we have a right and a responsibility to speak. Then follows the National Exposition of Chemical Industries.

For this great gathering many forces are working to insure its being an historic occasion. The railroads are coöperating to diminish the cost of travel. The Trunk Line Association and the South Eastern Passenger Association are offering reduced rates under the certificate plan (for important details concerning this feature see page 734 of this issue). It is hoped that other railway associations will soon take similar action. Chemists from the Pacific Coast will have the benefit of the regular summer tourist rates.

Not only are the hotels in New York City anxious to accommodate as many as possible, but Columbia University, in order to make sure that all will be provided for, will open its dormitories at the very low charge of $1.50 per day or $10.00 for the entire period. This arrangement is particularly fortunate in view of the fact that practically all of the meetings will be held in the lecture rooms of the University. A glimpse at the preliminary program, almost completed, shows an unusual assemblage of individual papers and symposiums of far-reaching importance. Secretary Hoover will be warmly welcomed, for his is a vitalizing touch wherever it falls.

For the first time the Chemical Exposition will display its exhibits on one great floor, with a larger number of exhibitors than in any previous year. At last the management will be in position to provide for lectures, addresses, and industrial movie films, a hall adequate in size and which, while in the same building as the exhibits, will be sufficiently removed to enable a thoughtful and attentive hearing of the subjects presented.

So much from the optimistic standpoint. But there is a graver reason which calls upon every chemist, no matter what the sacrifice, to make himself a personal part of this meeting. The feeling that a crisis is upon us cannot be set aside. Let us look the situation squarely in the face. To-day chemists of standing throughout the country are out of positions and this year's graduates from our universities find but few openings available to them. Of course we must expect to take our share of the generally low conditions in all lines of industry, but to the nation which is chemically farsighted such times should be marked by most strenuous research efforts in preparation for the swing of the economic pendulum back to the upward curve of industrial activity. No, there are deeper and more insidious reasons for this lack of employment of chemists. Two of these stand out preeminent. First, the chemical industry is being exploited by capital to-day in some quarters in a way which indicates no conception of the value of the scientific and technical men in such an industry, but rather suggests the tricks of a horse trader who rations his stock on carefully administered doses of arsenic preparatory to a quick sale. On this point we expect to write much more specifically in a subsequent issue. Secondly, the legislative issue trembles in the balance. Strange indeed is it that an industry which served this country so well during the critical days when millions of American young men were being hastily transported to the front to stay the assault of the German armies upon our very civilization, should now be blackguarded by those who sought to hold us back from that great conflict—and yet find followers sufficient to defeat legislation whose sole purpose is to preserve the industry as a permanent asset to the nation. And such a following! The Democrats casting aside the admonition of former President Wilson in two annual messages, and plainly for party politics, join forces now with the American Protective Tariff League, while the latter is evidently led by the ready chameleon Mr. Metz and in a subterranean way by the agents of the Badische Company. Every political trick known is being tried by those who lead the opposition, even while flaunting a flag of fair but hypocritical intentions. So brazen has become the attack that possibly their methods may yet prove a boomerang. It is time that the voice of American chemists should be heard in all of this turmoil. No action of the Committee on National Policies can take the place of the united voice of our members in national gathering assembled. It is time for action. Come on!

Have You Done Your Share?

"The elements of national defense are now the sum total of all the economic resources of the country plus all the man power. In time of imminent danger, the mobilization of a thousand chemists might be infinitely more important than the mobilization of a million troops." This definite conviction is expressed by Frank I. Cobb, the vigorous editorial writer of the New York *World*, in an article on the "Economic Aspects of Disarmament" in the August number of the *Atlantic Monthly*.

Scarcely had the ink dried upon that printed page when the House of Representatives turned down the recommendation of its Ways and Means Committee and defeated the coal-tar chemical limited embargo feature of the Fordney tariff bill by a vote of 208 to 193.

The outcome of that vote was a great surprise, for it was felt that after the careful study given by the Committee to this intricate and technical subject its recommendation would be accepted. But it was not, and thereby the chemical industry of America has been seriously jeopardized. While realizing that the particular link in the chemical industry adversely affected by this vote is not relatively the most important as to tonnage and value of output, nevertheless it is in this industry that proportionately the greatest number of chemists are utilized and it is for this branch of the industry that a large part of the young chemists in our universities are now in training. The industry calls for supplies of chemicals from all other lines and unquestionably it represents that part of our industry most intimately bound up with national defense. Strike down the coal-tar chemical industry and there will be a fatal slump all along the line in matters chemical. The mobilization of Mr. Cobb's "a thousand chemists" may become a difficult matter in such a contingency.

It is worth while, therefore, that the unfavorable vote in the House be analyzed, in order to see if the situation may not yet be saved.

The vote was upon an amendment by Congressman Frear of Wisconsin to strike from the bill the embargo section. This Congressman's fight against the embargo was just as vigorous as was his support, before our entry into the war, of the McLemore resolution which would have prevented American citizens from sailing on ships bearing munitions, and as was his opposition to the declaration of war against Germany and the passage of the draft bill after we had entered the war. He was well qualified for leadership. To his support he drew 112 Democrats, all except four from Louisiana, and 95 Republicans.

The vote of the Democrats was evidently for some reason of party politics. The votes of the 95 Republicans constitute the interesting problem. On what grounds did they bolt the recommendations of their Committee? Did they understand fully the significance and the importance of this industry to our country? For this last question we chemists are responsible. Did we do our part in making this clear to our Congressmen? Did we do anything in the districts concerned to arouse and enlighten public opinion on this vital matter? If not, then it is still up to us to do quickly everything in our power to make good the shortcomings of the past. Vacations are pleasant and work in the laboratory is delightful, but unless public opinion is quickly aroused these pleasant and delightful affairs may be of little interest to those of us who were once chemists.

Here is the list by states of the 95 Republican Congressmen who voted for the Frear amendment. Is your Congressman on this list?

CALIFORNIA
Barbour
Nolan

ILLINOIS
Fuller
Gorman
King
McKenzie
Michaelson
Sproul

INDIANA
Benham
Elliott
Hickey
Kraus

IOWA
Boies
Dowell
Haugen
Hull
Kopp
Ramseyer
Sweet

KANSAS
Anthony
Hoch
Little
Strong
White

KENTUCKY
Ogden
Robsion

MAINE
White

MARYLAND
Blakeney

MASSACHUSETTS
Underhill

MICHIGAN
Cramton
Woodruff

MINNESOTA
Anderson
Clague
Davis

MISSOURI
Hukriede
Lawrence
Roach

MONTANA
McCormick

NEBRASKA
Andrews
Evans
Kinkaid
McLaughlin
Reavis

NEVADA
Arentz

NEW HAMPSHIRE
Burroughs
Wason

NEW YORK
Ansorge
Chandler
Fish
Kline
Rossdale
Ryan

NORTH DAKOTA
Burtness
Sinclair
Young

OHIO
Cable
Fitzgerald
Foster
Gahn
Knight
Moore
Morgan
Norton
Ricketts
Speaks

OKLAHOMA
Gensman
Herrick

OREGON
Sinnott

PENNSYLVANIA
Burke
Connell
Connolly
Coughlin
Gernerd
Kline
Shreve
Rose
Strong

RHODE ISLAND
Burdick
Kennedy

SOUTH DAKOTA
Williamson

TENNESSEE
Brown
Reece
Scott

WASHINGTON
Summers

WEST VIRGINIA
Rosenbloom

WISCONSIN
Beck
Browne
Cooper
Frear
Kleczka
Lampert
Nelson, A. P.
Nelson, J. M.
Stafford
Voigt

The matter may still have to go to the Conference Committee and his support may be needed, and perhaps this vote indicates that your senators also do not appreciate the gravity of the situation.

Have you done your share, fellow chemist? Better vigorous action now than vain regrets later.

Restoration in Poland

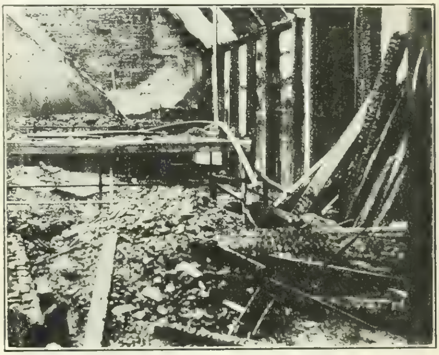
The restoration of the University of Louvain has made a deep appeal to the whole world and particularly to Americans. It is good to know that from the ashes of that venerable institution so ruthlessly destroyed there is to arise another and even greater institution. Yet we must remember that Belgium is not alone in its sorrow and suffering.

Poland must be restored as a vigorous nation. The struggle for restoration is intense, for it was ravaged first by the Russians and then by the Germans.

Since receipt of the following letter it has been learned that a committee is being organized which, in coöperation with the Polish Consulate, will endeavor to raise funds to relieve this distressing situation. Keep your hearts and purses open.

May I not tell you something of the plight of the men of science in Poland. Here in the United States we can hardly realize how difficult their life is and under what wretched conditions they are trying to do productive work. Since the very beginning of the war they have been without the very necessary scientific books and technical periodicals from abroad.

The universities have been pillaged and stripped by both the Germans and Russians—sometimes even the buildings have been destroyed, as in the case of the chemical laboratory of the University of Posen. I enclose a photograph (showing this destruction) that was sent to me together with a letter of petition from the faculty begging me to help them to rebuild and equip a new laboratory.



From Lemberg, my husband, who is professor of geophysics, writes continually of the lack of means at the disposal of the faculty of the University. May I not translate from one of his recent letters?

"Oh how I long to have a laboratory, a good library, the instruments necessary for observations, and the means to publish!

"I need chemical equipment to make analyses of air and rain-water, actinometers, pyrheliometers to measure solar radiation, an electric oven, a pendulum, sufficient at least to make field observations. I must have glassware and chemical reagents, platinum, a balance, a microscope.

"Just think all this equipment would not cost more than eight thousand dollars. Yet I will have to struggle all the rest of my life and expend all my efforts that perhaps my successor may have the necessary means of working and producing. It is discouraging. But when I think of the financial situation of the government I can see no issue. It is hardly possible for you to realize how difficult the situation is here.

"Poland is expected to be productive but no one stops to think of the fact that to produce it is necessary to have the means of production.

"It is perhaps natural that America should be tired of Europe, and does not wish to learn of the miseries that exist here, but still . . . . . "

Is there no way for us to finish that sentence? Can we not extend a friendly helping hand to these men who want so badly to do and who could do if they had the means?

Sincerely,
(*Signed*) JANE ARSTOWSKA.

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

The Water Resistance of Treated Canvas during Continuous Exposure to Weather[1,2]

By F. P. Veitch and T. D. Jarrell

LEATHER AND PAPER LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

This investigation is part of the work of the Bureau of Chemistry on the waterproofing of cotton duck, and was undertaken for the purpose of determining the actual relative water resistance in service of waterproofing preparations developed in the Bureau for treating cotton duck for outdoor use. In addition to the exposure tests, laboratory tests were also made, both on the new, recently treated canvas and again after the canvas had been exposed for a year, and the results and ratings obtained in these tests are also included.

A paper by Holman, Levine and Jarrell[3] deals with the classes and selection of cotton duck suited for farm and other outdoor uses, gives directions for its proper care, describes briefly the different types of waterproofing processes most commonly used, and gives formulas which were developed for increasing the serviceability of canvas. The laboratory methods employed in testing the water resistance of canvas have been published.[4]

The present paper is a detailed report on the water resistance exhibited in actual service of various treatments which were studied in the broader investigation on the waterproofing and mildew proofing of cotton duck.

Little has been published on the serviceability, water resistance, or strength of treated or untreated canvas after exposure for a considerable time to outdoor weather. Turner, in his paper on "The Influence of Atmospheric Exposure on the Properties of Textiles,"[5] which appeared about a year after this investigation was begun, has presented results on the water resistance and strength of weathered fabrics which had been treated to increase their water resistance with (1) oils, (2) cupra-ammonium, (3) bitumens, and (4) basic aluminium acetate. Water resistance was determined by the funnel test, and the conclusions drawn were:

Oil treatment—"Initially the proofed fabric is satisfactory as regards water tightness, but this property is considerably impaired on continued exposure."

Cupra-ammonium treatment—"The water tightness of the proofed fabric was satisfactory before exposure; the action of weathering, however, soon caused the material to become leaky and this proofing also was therefore deemed unsatisfactory."

Bitumen proofing—"The water tightness results were peculiar in that they pointed to a gradual improvement in water tightness on exposure."

Basic aluminium acetate—"The water tightness was satisfactory initially and for some time subsequently, but tended to diminish gradually if the exposure was prolonged."

PREPARATION AND APPLICATION OF MATERIALS

The formulas used in this investigation are the outgrowth of much preliminary work and were designed not alone to show what are the most water resistant combinations, but also to show experimentally which of the more commonly used materials are valueless for increasing the water resistance of canvas. A description of the treatments or formulas used in this study, numbered from 1 to 18, inclusive, will be found in Table II.

The formulas were prepared and applied as follows: The solid materials were weighed out in proper proportions and melted carefully at as low a heat as possible, with constant stirring. When the mixture was completely melted, it was poured with constant stirring into a mixture of 2 parts by volume of gasoline and 1 part by volume of kerosene, adding 2 lbs. of the solid material to 1 gal. of the solvent.

Lead oleate, which is a constituent of several of the mixtures, is but slightly soluble in this solvent, but it will remain suspended in the liquid if it is completely melted with the other ingredients, and the solvent is vigorously stirred while the mixture is slowly poured into it, and if the solution is then vigorously shaken or stirred at intervals over a day or so.

The hard vegetable or mineral waxes which were used in all the formulas, excepting 7, 8, 11, 12, 13, and 16, separated out when the solutions cooled. It was necessary to warm these solutions slightly by placing them in open containers in a bucket of hot water just before applying to the canvas. The amorphous mineral wax was a soft mineral grease obtained as a by-product in refining cylinder oil stocks, and was very similar to the product generally known as dark petrolatum. It was, however, more viscous and had a higher melting point. The paraffin was an ordinary scale wax having a melting point of 122° F. The beeswax was pure "yellow refined." The copper and lead oleates were technical grades. The Bermudez asphalt was the ordinary refined grade, having a penetration of 18, while the petroleum asphalt used in Formula 13 had a melting point of 264° F. and a penetration of 17. The ring and ball method[1] was used for determining the melting point of these materials. Penetration was determined by Hubbard's method,[2] and the load, time, and temperature used were 100 g., 5 sec., and 25° C., respectively.

All tests were made on strips 12 ft. long and 15 in. wide,

---

[1] Received April 20, 1921

[2] Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921

[3] U. S. Department of Agriculture, *Farmers' Bulletin* **1157**.

[4] THIS JOURNAL, **12** (1920), 26.

[5] *J. Soc. Dyers and Colourists*, **36** (1920), 165.

[1] *Proc. Am. Soc. Test. Materials*, **17** (1917), I, 811.

[2] U. S. Department of Agriculture, *Bulletin* **691**.

TABLE I—WATER RESISTANCE OF VARIOUS SECTIONS OF THE TREATED PAULIN AS INDICATED BY CONDITION OF UNDERSURFACE OF BAG SECTION AFTER RAIN
(Dry, except as otherwise noted. W means Wet; D means Dripping)

Observation Number	Date of Observation	Hours Water in Bag	TREATMENT NUMBER																		Blank 12 Oz. U S Standard Army Gray Duck	12-Oz. U. S. Standard Army Mineral Khaki Duck
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	9-11-'19	16	–	–	–	D	D	D	D	D	–	D	–	D	–	D	D	D	W	D	D	–
2	9-23-'19	9	–	–	D	D	D	D	D	D	–	D	–	D	–	D	D	D	W	D	D	D
3	10- 3-'19	19	D	–	–	D	D	D	–	D	–	D	–	–	–	D	D	D	D	D	D	D
4	10-12-'19	18	D	–	D	D	–	D	–	D	D	–	–	–	–	D	D	D	W	D	D	D
5	11-30-'19	26	–	–	–	W	–	–	–	–	–	–	–	–	–	D	–	–	–	D	D	D
6	2-13-'20	18	–	–	–	–	–	–	–	–	–	–	–	–	–	D	–	D	–	D	D	D
7	2-22-'20	24	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	D	D	D
8	2-24-'20	65	–	–	–	W	–	W	–	–	–	–	–	–	–	D	–	–	–	D	D	D
9	4- 2-'20	17	–	–	W	D	–	W	–	–	–	–	–	–	–	W	D	W	D	D	D	D
10	4- 4-'20	12	–	–	–	–	–	–	–	–	–	–	–	–	–	D	–	–	–	D	D	D
11	4-17-'20	14	–	–	–	–	–	–	–	–	–	–	–	–	–	W	–	–	–	D	D	D
12	4-18-'20	44	–	–	–	D	D	D	–	–	–	–	–	–	–	–	D	–	–	D	D	D
13	5- 8-'20	20	–	–	–	–	–	D	–	–	–	–	–	–	–	–	D	–	–	D	D	D
14	6- 5-'20	29	–	–	D	D	–	D	D	–	–	D	–	–	–	D	–	D	D	D	D	D
15	6- 6-'20	50	–	–	D	D	D	D	D	–	–	D	–	–	–	–	D	D	D	D	D	D
16	6-21-'20	23	–	–	W	D	D	D	D	D	W	D	–	–	–	–	D	D	D	D	D	D
17	9- 6-'20	3	D	–	D	D	D	D	W	W	–	D	–		–	D	D	D	W	D	D	D
18	10-28-'20	16	–	–	–	–	–	–	–	–	–	–	–	–	–	W	–	–	–	D	D	D
19	12-23-'20	20	W	–	–	–	–	–	D	–	–	–	–	–	–	D	–	D	–	D	D	D
Times dry			15	19	12	7	12	7	12	13	17	12	19	17	19	5	9	8	10	0	0	1
Times wet			4	0	7	12	7	12	7	6	2	7	0	2	0	14	10	11	9	19	19	18
Per cent efficiency			79	100	63	37	63	37	63	68	89	63	100	89	100	26	47	42	53	0	0	5.0

Note: Observations in May, June, and July 1921 show that the treatments have maintained their water resistant qualities, actually and relatively, except that Number 10 has risen to the eighth and Number 3 has fallen to the eleventh position.

cut from the same bolt of 12-oz. gray United States standard army duck, having the following weight and construction:

	Threads per Inch		Ply	
Wt. per Sq. Yd.	Warp	Filling	Warp	Filling
15.2 oz.	46	35	3	3

In each case, one coat of the preparation was applied with an ordinary paint brush to one side only, and the weight of the duck was increased from 25 to 30 per cent by each treatment.

The waterproofing mixtures were thoroughly stirred just before and during application so that all the undissolved material would be kept uniformly suspended.

A portion of each strip was reserved for laboratory tests. The remaining portions, measuring 9 ft. by 15 in., together with strips of the untreated duck and a strip of 12-oz. United States standard army mineral khaki duck, were sewed together to make a paulin.

EXPOSURE CONDITIONS

The paulin was attached to a wooden frame and exposed to the weather in the open country continuously from August 14, 1919, until about the same date the following year. The frame was set level from end to end, faced the east, and was designed to give all possible types of outdoor exposure that are likely to occur in the use of canvas as wagon covers, goods covers, tents, awnings, etc. The paulin was loosely but smoothly stretched on this frame in such a way that 3.5 ft. of each treatment were level, and 3.5 ft. were inclined at an angle of 30°, while at the bottom of the inclined section the paulin was made to form a bag section about 6 in. deep.

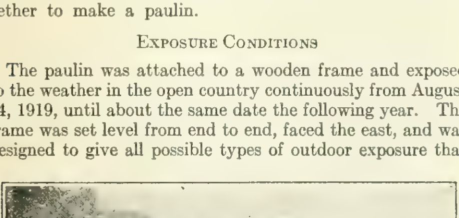


FIG. 1—SHOWING HOW THE PAULIN WAS EXPOSED

Rain falling on the canvas, both on the level and the inclined sections, ran down and collected in the bag section, where it was allowed to remain for some time, often from 2 to 3 days, before emptying. Both in the level and the sloping sections the canvas touched a 2-in. strip of wood and also a board 12 in. wide, while in between these boards the underside was exposed to the air, Fig. 1. In this way, it was expected to show the effect of contact with objects on the underside of the canvas, and also the penetrating effect of rain on both the unsupported and the supported canvas. The paulin was tied on the frame but was free to move with the winds, which lifted it, subjecting it to such strains and motion as would occur on a moving load. The paulin remained on the frame continuously from August 14, 1919, until July 2, 1920, when it was rolled up damp and stored away in a cellar until August 30, 1920, in order to allow it to mildew (which it had not done before), after which it was again placed on the frame. Sections were cut from the upper flat end and from the lower end of each strip of the paulin at this time (August 30, 1920) for laboratory tests.

Frequent observations were made on all sections of the paulin either during rain or immediately thereafter, and the condition of undersurface of the bag section was carefully noted and recorded, as well as any indication of the undersurface becoming wet or dripping either directly over the boards or between them. The number of hours the water had stood in the bag was also noted. The height of the water in the bag was practically the same in all sections at the time of observation, and ranged from 1.5 to 3.5 in. in depth at different inspections. The water resistance of the bag section of the paulin is expressed as percentage efficiency, and the figures were obtained by dividing the number of times the undersurface was dry by the total number of observations, and multiplying by a hundred.

In ascertaining by laboratory methods the water resistant qualities of the different treatments, the modified funnel test and the modified spray test, as devised by Veitch and Jarrell,[1] were employed, and the treatments were rated on a basis of 10 in accordance with the scale outlined in their article.

DISCUSSION OF RESULTS

SMOOTH PORTION OF PAULIN—Observations were made on the undersurface of the level and inclined sections of the paulin during or directly after fifteen different rains from August 17, 1919, to December 23, 1920.

---

[1] *Loc. cit.*

The undersurface of the strips treated with Formulas 1 to 17, inclusive, was never found to be wet, either where the underside was exposed to the air or rested on the strips or boards, nor were the boards ever found to be wet or damp to the touch.

The strip on which Formula 18 was applied, however, was wet at the first two inspections (August 17, 1919, and September 10, 1919), but the boards were dry on the following inspection (September 23, 1919), and all subsequent observations, even though the rain on September 23, 1919, was much heavier than the one on September 10, 1919.

The undersurface of the strip dyed mineral khaki was dry at all inspections up to October 28, 1920, when the boards were found to be wet. The boards were also wet at the next observation on December 23, 1920. It is of interest to note that the khaki strip would drip at every rain if the undersurface were slightly rubbed with the hand during a rain. Rubbing was tried on all the strips during various rains, one of which was a very severe one (July 2, 1920). Treatments 1 to 17, inclusive, did not become wet even under this rubbing, which to a degree was similar to the friction and contact that might exist between the load on a moving wagon and the canvas covering it.

The undersurface of the untreated strip was dry at the first inspection (August 17, 1919, 3 days after placing on frame), but was wet on the second (September 10, 1919, 1 mo. after placing on frame), and at all subsequent observations.

BAG PORTION OF PAULIN—The water resistance of the various sections of the treated paulin, as indicated by the condition of the undersurface of the bag section, is given in Table I. There were nineteen observations in all, from September 11, 1919 (about 1 mo. after first exposing) until December 23, 1920. In each case the water had been in the bag from 3 to 65 hrs. when the inspection was made.

It will be seen from Table I that the undersurface of the untreated section dripped at every rain. The khaki duck dripped every time except at the first observation on September 11, 1920. That is, the resistance of mineral dyed canvas, of this weight and weave, to a layer of water is not materially greater than the resistance of undyed duck of the same weight and weave. This behavior probably explains why the laboratory funnel test, as shown in Table II and Fig. 2, gives the khaki duck a rating of 8 before exposure and a 0 rating after exposure.

There is no outstanding explanation of why a treatment that renders the canvas practically waterproof in the bag section during one rain lets the water through readily at another rain. There is a wide fluctuation in the water resistance of most of the treatments, which probably indicates not only the relative water resistance of these treatments but probably also indicates normal irregularities which cannot be avoided in testing, except in those extreme cases where there is complete waterproofing or no waterproofing whatever. It is believed, therefore, that the value and effectiveness of the several treatments are very accurately indicated by the figures for "per cent effectiveness" calculated from nineteen observations extending over 15 mo. It will be noted that Treatments 2, 11, and 13 are rated at 100 per cent, Treatment 18, at 0 per cent, and that the other treatments range from 89 to 26 per cent. It will also be noted, from Table I, that the water resistance of all treatments was apparently as good after exposure for 1 yr. as when the paulin was first placed on the frame.

These treatments have been subjected to exceptionally severe conditions, and it would appear from the results obtained that the water resistance of 12-oz. United States standard army gray duck, treated with these waterproofing preparations, may be expected to endure for at least 18 mo. of continuous exposure, in the form of wagon tops, tents, truck and automobile covers, awnings, etc. For use where exposure is not continuous the treatments may reasonably be expected to be more durable. A subsequent paper will deal with the strength of the fabric under each treatment.

TABLE II—RESULTS ON WATER RESISTANCE BY LABORATORY TESTS AND EXPOSURE TEST

			LABORATORY TESTS				
			Before Exposure		After Exposure		During Exposure
No.	TREATMENT	Per cent	Funnel Test (Rating)	Spray Test (Rating)	Funnel Test (Rating)	Spray Test (Rating)	Bag Sections (Rating)
1	Amorphous mineral wax Beeswax	85 15	9	9	4	8	7.9
2	Amorphous mineral wax Beeswax Lead oleate	65 15 20	10	10	10	10	10.0
3	Amorphous mineral wax Beeswax Copper oleate	65 15 20	9	9	6	9	6.3
4	Amorphous mineral wax Paraffin	75 25	6	9	2	8	3.7
5	Amorphous mineral wax Paraffin Lead oleate	60 20 20	5	9	4	9	6.3
6	Amorphous mineral wax Paraffin Copper oleate	60 20 20	2	8	1	8	3.7
7	Amorphous mineral wax Lead oleate	75 25	9	10	6	10	6.3
8	Amorphous mineral wax Bermudez asphalt	85 15	9	8	6	8	6.8
9	Amorphous mineral wax Beeswax Bermudez asphalt	75 10 15	10	10	9	10	8.9
10	Amorphous mineral wax Paraffin Bermudez asphalt	60 25 15	9	10	6	9	6.3
11	Amorphous mineral wax Lead oleate Bermudez asphalt	60 25 15	10	10	9	10	10.0
12	Amorphous mineral wax Copper oleate Bermudez asphalt	60 25 15	9	9	9	9	8.9
13	Wool grease Lead oleate Petroleum asphalt	25 15 60	10	10	10	10	10.0
14	Amorphous mineral wax Japan wax	75 25	4	10	4	7	2.6
15	Amorphous mineral wax Ceresin	75 25	6	9	3	8	4.7
16	Amorphous mineral wax Rosin	75 25	1	6	0	6	4.3
17	Amorphous mineral wax Candelilla wax	90 10	9	9	0	8	5.3
18	Paraffin Rosin	85 15	0	4	0	7	0
Blank	12-oz. U. S. standard army gray duck (untreated)		0	0	0	0	0
	12-oz. U. S. standard army mineral khaki duck		8	5	0	4	0.5

RESULTS OF LABORATORY TESTS

Table II gives the results on water resistance of the several treatments by the modified funnel and the modified spray tests. These tests were made both on portions of the treated strips taken before exposure and on pieces cut from the strips after exposing for approximately 12 mo. (pieces cut from paulin August 30, 1920). For comparison there is also included in this table the water resistance ratings on a basis of 10 of the various sections of the paulin as indicated by the condition of the bag section, as already shown in Table I.

Fig. 2 is a graphic presentation of the results included in Table II, omitting the results by the modified spray test. In this figure the treatments are given in the descending order of their effectiveness as determined by the exposure test. The method of calculating the ratings has already been explained.

It will be noted from Fig. 2 that Treatments 2, 11, 13, 9, and 12 have a rating between 9 and 10 by the funnel test before and after exposure, and between 8.9 and 10 by the exposure test. These are the five best treatments of those

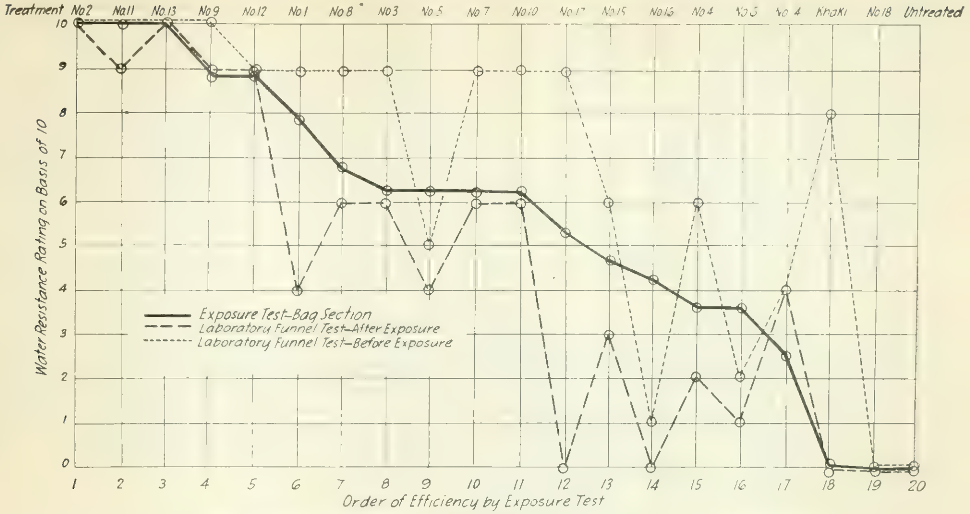


FIG. 2—CHART SHOWING THE RESULTS OF WATER RESISTANCE BY EXPOSURE TEST AND BY LABORATORY FUNNEL TEST BEFORE AND AFTER EXPOSURE

studied. It is also seen that Treatment 18 and the untreated duck have ratings of 0 by both the funnel and exposure tests, while the mineral dyed khaki which has a service rating to standing water of practically zero (0.5) has, when new, a rating of 8, and after a year's exposure a rating of 0 by the funnel test.

In general, the average rating on the bag sections by the funnel test before exposure (6.8) is higher than by the exposure test (5.6), while the average rating by the funnel test is slightly lower (5). The ratings by the spray test average 8.2 before exposure and 7.9 after exposure, showing practically no difference. It is of interest to note that by the spray test Treatment 18 gets a rating of 4 before exposure, and 7 after exposure. It will be recalled that in this treatment the undersurface of the smooth sections was wet at the first two observations (August 17, 1919, and September 10, 1919), but remained dry at all subsequent observations, as a result possibly of a more thorough coating of the fibers of the canvas by the rosin and paraffin after exposure. The results by the spray test are in harmony with those obtained by exposure on the flat section.

While in most cases there exists no very close relation between the funnel test before exposure and the result of actual exposure, it is believed that the modified funnel test, if carried out according to directions, is the most reliable single test yet developed to differentiate between effective and ineffective waterproofing treatments for cotton duck.

It should be remembered, however, that 12-oz. United States standard army gray duck was used for all the experiments, and it may be that the results obtained are not directly applicable to any other grade or weight of duck. However, in the light of available data, it is assumed that if the treatments herein described are applied in the same way to other ducks of various weights and constructions and the method of exposure is the same in all cases, the waterproofing treatments will fall in approximately the same order as found in these experiments.

CONCLUSIONS

The following general conclusions may be drawn as to the water resistance of these treatments when applied to 12-oz. United States standard army gray duck and when the treated duck is exposed to the weather, as described.

1—All of the treatments increase the water resistance of canvas sufficiently for use as permanent tops or covers which lie smooth. Such covers are wagon tops, shock and hay covers, tents, and awnings.

2—When lead oleate is included in the formulas, the water resistance is increased. (Compare Formulas 1 with 2, 4 with 6, and 8 with 11.) All three of the treatments having a rating of 100 per cent contained lead oleate.

3—Bermudez asphalt is also an effective constituent in these formulas, fully as good as lead oleate. (Compare Formulas 7 with 11, 4 with 10, and 1 with 9.) Other experiments indicate that there is no material difference between Bermudez asphalt and petroleum asphalt.

4—Copper oleate is not as effective a waterproofing agent as lead oleate. (Compare Formulas 2 with 3, 5 with 6, and 11 with 12.)

5—Beeswax is a much more effective waterproofing agent than any of the other hard waxes used, including paraffin and ceresin. (Compare Formulas 1, 2, and 3 with 4, 5, and 6, respectively; 1 with 14, 15, and 17; and 9 with 10.)

6—Amorphous mineral wax is a better waterproofing agent than paraffin. (Compare Formula 16 with 18.)

7—Wool grease is a useful constituent in formulas containing other waterproofing agents. (See Formula 13.) Other results indicate that the substitution of amorphous mineral wax for wool grease in this formula does not decrease its water resistance.

The following conclusions are drawn from the laboratory tests:

8—Both the funnel and spray tests applied to new, treated duck indicate higher water resistance than is actually found in service.

9—Water resistant treatments for 12-oz. United States standard army duck giving a rating of 6 or better by the spray test have proved serviceable for smooth covers, such as awnings, wagon tops, stack and hay covers.

10—The waterproofing treatments which have proved most serviceable on 12-oz. United States standard army gray duck have also given high results by the funnel test. However, not all treatments showing a high rating by the funnel test have proved highly serviceable in those cases where water lay for some time on the canvas.

11—When a treatment secured the maximum rating by both the funnel and the spray tests, it also received a high rating (8.9 or better) in the service test.

12—After a year's exposure, the ratings by the funnel test, with the exceptions of Treatments 2, 9, 12, 13, and 14, were lower than the service ratings.

13—After a year's exposure the ratings by the spray test were still high and were in general harmony with the observations made on the sloping and flat sections of the canvas.

14—In the formulas used, paraffin, Japan wax, ceresin, candelilla wax, and rosin were not effective waterproofing materials on canvas. Although formulas containing these materials may have rated high by both the funnel and the spray tests when the canvas was new, they lacked durability.

15—Neither the funnel test nor the spray test alone is an infallible indication of the serviceability of a waterproofing treatment for canvas.

The Effect of Certain Fire-Proofing Solutions on Cotton Fabric[1,2]

By R. L. Sibley

216 South Broad St., Elizabeth, N. J.

The high inflammability of fabrics has been the cause of many serious accidents, and attempts have for a long time been made to impregnate these materials in such a manner as to guard against this danger. Many compounds have been used for rendering the materials uninflammable, but in every case the impregnated fabrics have been tested only for the effect of flame by holding the treated cloth in the flame of a candle or some other suitable heating agent and ascertaining the relative ease of combustion as compared with that of the untreated materials.

There has been collected a very considerable amount of data regarding the quantities of various substances needed to render the materials uninflammable, such, for example, as the least strength of solution and least quantity of anhydrous salt or compound necessary for rendering 100 parts of cellulose noncombustible, but the effect of these solutions on the wearing qualities and especially on the strength of the fabric was not known. This effect can be ascertained readily by determining the breaking strength of samples of treated fabric and comparing this value with that of the untreated materials of the same moisture content.

Method of Testing Breaking Strength

Samples of tire duck fabric were used for these tests. One sample was a fabric weighing 18.5 oz. to the sq. yd., while the other weighed 36 oz. to the sq. yd. Test pieces of fabric approximating 6 in. in length and 2.25 in. in width were cut, and were raveled until there remained 23 threads of the heavy fabric and 46 threads of the light fabric as the width of the respective pieces. These corresponded closely to a test piece 1 in. in width, in each of the two cases. The test pieces were boiled in the solution to be tested for 15 min. in order to obtain a complete impregnation, lightly wrung out, and hung up to air-dry for 3 days before testing. Cotton fabric normally contains a considerable amount of moisture, and it is, of course, a well-known fact that absolutely dry fabric is very hygroscopic. The method of drying the samples to the same moisture content was chosen in order to eliminate any possibility of variability due to the effects of the presence of different amounts of moisture. This can safely be assumed to be the case after 3 days' drying of the completely wetted samples at room temperature, for by that time the moisture content of the fabric and of the atmosphere will be in equilibrium. Inasmuch as all pieces (with the exception of two tests which were repeated) were prepared on the same day, dried under identical conditions for the same length of time, and tested on the same day, the effect of humidity on the fabric need not be considered. The breaking strengths of these test pieces were determined in a Scott testing machine, with the results given in lbs. per in. width of fabric.

A control sample was boiled for 15 min. in distilled water to saturate with water, air dried, and tested under the same conditions.

Solutions Used for Tests

The solutions used for the impregnation of the fabric were as follows:

A—The fabric was boiled in a saturated solution of $Al_2(SO_4)_3.18H_2O$ for 15 min., dried in an oven at 80° C., boiled for 15 min. in a saturated Na_2CO_3 solution, allowed to dry, and tested. Alum and aluminium carbonate are mentioned in several places as recommended by Gay-Lussac as among the best known substances for preventing the inflammability of fabrics.

B—This solution is known as Gleichmar's receipt[1] and is made from:

	Parts
NH_4Cl	40
$Na_2B_4O_7$	10
$NaCl$	5
H_2O	300

C—C. A. Martin's fireproof dressing[2] for coarse fabrics is composed of:

	Parts
NH_4Cl	15
$Na_2B_4O_7$	3
H_3BO_3	6
H_2O	300

D—Fifteen per cent sodium tungstate ($Na_2WO_4.2H_2O$).[3]

E—Sulliot and David's receipt[4] is as follows:

	Grams
$Na_2B_4O_7$	50
Glucose	25
H_2O	425

F—Three and five-tenths per cent sodium tungstate.

G—Pateras' fireproof dressing[5] is prepared as follows:

	Grams
$Na_2B_4O_7$	60
$MgSO_4$	30
H_2O	400

Results of Tests

The breaking strength of the samples of treated fabrics tested in the manner indicated were as follows:

---

[1] Received February 18, 1921.

[2] The work described in this paper was carried out in the Research Laboratories of the Goodyear Tire and Rubber Co., and the thanks of the author are hereby expressed for permission to publish these results.

[1] Polleyn, "Dressings and Finishings for Textile Fabrics and Their Application," 206.

[2] Polleyn, 207.

[3] Lochtin, *J. Soc. Chem. Ind.*, **13** (1894), 512.

[4] Polleyn, 209.

[5] Polleyn, 207.

	HEAVY FABRIC				LIGHT FABRIC			
	1	2	3	Av.	1	2	3	Av.
Control	302	288	286	292	212	188	180	193
A[1]	...	...	...	...	...	...	...	...
B	200	194	184	193	170	182	185	179
C	292	305	324	307	138	124	160	141
D	444	442	468	451	190	188	204	194
E	157	150	164	156	144	148	154	149
F	225	264	225	241	210	198	188	199
G	208	220	200	209	178	155	158	164

[1] No breaking tests could be obtained on the fabric treated with Solution A, inasmuch as the fabric had been so seriously affected by the alum as to be easily torn apart in the fingers.

Results with Tests C and D are contradictory in indicating a greater tensile strength in the case of the treated heavy fabric than the control possessed, while the effect on the treated light fabric was a weakening action with the first material and no perceptible effect with the sodium tungstate. This was probably due either to some error in obtaining the breaking strengths of the samples or to some unknown and unavoidable difference (*e. g.*, air currents) in the drying of the test pieces. A second series of tests was carried out (in comparison with a new control) under the same conditions as the first tests but on a different day and consequently with different humidity conditions. The results, which are more in accord with the first series obtained, are as follows.

	HEAVY FABRIC				LIGHT FABRIC			
	1	2	3	Av.	1	2	3	Av.
Control	316	333	304	318	229	212	228	223
C_1	209	200	200	203	188	215	184	195
D_1	250	238	292	260	230	216	200	215

CONCLUSIONS

1—Of the three types of fireproofing agents tested, sodium tungstate is shown to have the least effect on the breaking strength of the fabric and therefore the least weakening action.

2—Furthermore, a test of the fireproofing qualities of the solutions showed the 3.5 per cent solution of sodium tungstate to be practically as efficient as the stronger solution. This, then, is recommended as an excellent fireproofing agent for the impregnation of cotton fabric whose breaking strength and wearing qualities must not be materially weakened by the process employed.

The Use of Nitroglycerin Spent Acid as Charging Acid for Nitric Acid Stills[1]

By S. G. Norton

HERCULES POWDER CO., WILMINGTON, DELAWARE

The method of disposing of spent acid described in this paper has been known and used in America for several years. The spent acid, as received from the nitroglycerin plant, containing approximately 75 per cent H_2SO_4 and 7.5 per cent HNO_3, was treated essentially as follows:

After standing in open tanks for 24 hrs. the spent acid was examined for free nitroglycerin. Any traces of the latter having been carefully skimmed off, the acid was drawn down into a mixing tank. Sufficient fuming sulfuric acid of approximately 108 per cent strength was added to bring the sulfuric content up to the desired percentage, a thorough air agitation being maintained during the addition and for some time thereafter. The resulting mixture, which was used to replace the usual 66° Bé. sulfuric acid for charging the stills, contained about 4.00 per cent of HNO_3.

After using the charging mixture containing spent acid for several months, it was noted that a consistently lower yield was obtained from the nitric acid plant than had been obtained previously. The nitrosyl content of the mixed acid made at the plant increased. Poor separations were obtained in the nitroglycerin operations. These difficulties increased cumulatively with each round of the acid through the system.

SMALL SCALE STUDY OF PROCESS

Since it appeared that the use of charging acid made from spents was of questionable advantage, a careful series of distillations was made on a laboratory scale to determine, so far as possible, what was taking place in the nitric stills where the spent acid charging mixture was used.

The apparatus used for the distillations consisted of a glass retort of about one-liter capacity, a condenser, and a receiver, all having ground connections. From the receiver the gases were drawn, under slight vacuum, through an absorption system consisting of three gas-washing bottles. The first two of these contained water, and the third a 5 per cent solution of sodium hydroxide.

All materials used were carefully analyzed. The acid and the various wash waters resulting from each distillation were also analyzed, tests being made for various substances which might affect the yield figure. The nitrate of soda used was uniform throughout the entire investigation, a large sample having been obtained and carefully blended at the beginning of the work. The acids used were also obtained in large enough quantity so that the same sample could be used throughout a series.

Three sets of distillations were made. The results of these distillations will be found in the table. The first set, in which straight 66° Bé. sulfuric charging acid and nitrate of soda were used in a ratio of 1:1 by weight, was carried out to determine what yield might be expected from the nitrate of soda under the conditions of the experiment. The average yield obtained was 99.13 per cent, calculated as total HNO_3.

For the second series, a charging acid was prepared from a sample of spent acid as received from the nitroglycerin operation, by mixing it with 108 per cent fuming sulfuric acid in the usual manner. The charging acid thus prepared showed the following analysis:

	Per cent
H_2SO_4	88.50
HNO_3	4.31

In charging the retort an additional weight of this charging acid was used, so as to have the ratio of sulfuric acid to soda the same as in the preceding series. It will be noted from the accompanying table that, while an average of 75.762 g. of HNO_3 was obtained, if we assume the same yield from the soda as the first series gave, *i. e.*, 99.13 per cent, 71.594 g. of the HNO_3 are accounted for. This leaves only 4.168 g. of HNO_3 obtained from the charging acid. Since 4.741 g. of HNO_3 were introduced in the charging acid, we have a yield on the latter of only 87.91 per cent.

A third series of distillations was made, in which charging acid prepared from a different sample of nitroglycerin spent was used. The analysis of this charging acid was:

	Per cent
H_2SO_4	88.08
HNO_3	4.68

While an average of 5.212 g. of HNO_3 was introduced in the charging acid in this series, only 4.281 g. were recovered.

---

[1] Received February 9, 1921.

a yield of 82.16 per cent. These yields are very much lower than would have been obtained if the spent acid had been denitrated in the usual manner.

The distillations made with spent acid charging mixture required a longer time for completion than did those made with straight charging acid. They were also distinguished by a copious and nearly continuous evolution of NO_2. An average of 2.75 per cent of the total yield was obtained as NO_2, as against 0.40 per cent where straight charging acid was used.

The yield not accounted for in the distillations made with spent charging acid was obtained in the form of NO, N_2O, and free nitrogen. Since these gases are not recoverable in practice, they constitute a serious loss when formed in large quantities.

CONCLUSION

As a result of the foregoing investigation, the use of spent acid for charging nitric stills has been abandoned at this plant. The usual recovery operation was resumed, and after the spent acid had been eliminated from the system the former satisfactory yields were obtained from the nitric acid plant.

							Per cent Yields		
KIND OF ACID	Total Yield as HNO_3[1] Grams	Yield NO_2 Grams	Grams HNO_3 Theoretically Possible from Soda Used	Grams HNO_3 from Soda with 99.13 Per cent Yield	Grams HNO_3 Theoretically Possible from Spent	Grams HNO_3 Actual Yield from Spent[2]	Total HNO_3	Actual HNO_3 Not Including NO_2	Total HNO_3 from Spent
Straight Charging (H_2SO_4, 92.44 per cent)	71.641	0.346	72.220				99.20	98.78	
	71.577	0.360	72.220				99.11	98.44	
	71.554	0.410	72.220				99.08	98.32	
AVERAGE..............	71.591	0.372	72.220				99.13	98.53	
Sample 1, Spent Charging (H_2SO_4, 88.50 per cent, HNO_3, 4.31 per cent)	75.758	1.498	72.220	71.594	4.741	4.164	98.44	95.83	87.83
	75.770	1.517	72.220	71.594	4.741	4.176	98.45	95.81	88.08
	75.758	1.314	72.220	71.594	4.741	4.164	98.44	99.15	87.83
AVERAGE..............	75.762	1.443	72.220	71.594	4.741	4.168	98.44	95.93	87.91
Sample 2, Spent Charging (H_2SO_4, 88.04 per cent, HNO_3, 4.63 per cent)	75.900	1.623	72.220	71.594	5.245	4.306	97.98	95.18	82.15
	75.869	1.706	72.220	71.594	5.195	4.275	98.00	95.05	82.30
	75.856	1.878	72.220	71.594	5.195	4.262	97.99	94.73	82.04
AVERAGE..............	75.875	1.736	72.220	71.594	5.212	4.281	97.99	94.99	82.16

[1] Total acidity calculated as HNO_3 minus nitric values for HCl and H_2SO_4.

[2] This figure represents total yield as HNO_3 (Column 2) minus the average actual yield from the soda used (Column 5). The latter is calculated as 99.13 per cent of that theoretically possible.

The Thermal Decomposition of Oil Shales. II_Determination of the Heat of Reaction Involved in Their Thermal Decomposition[1,2]

By Ralph H. McKee and E. E. Lyder

DEPARTMENT OF CHEMICAL ENGINEERING, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

The solution of the problem of the recovery of petroleum oils and other products from the so-called oil shales of this country must be based on exact information, such as the values of all the physical constants involved, a knowledge of the manner in which the oil-forming material decomposes, and information as to the character of the product obtained under varying conditions. Also, since it is apparently established that the only way to recover petroleum oils from shales is by thermal decomposition,[1,2,3*] a study of the heats involved and the primary effect of heat on the shale is evidently most essential to the intelligent development of the industry. It has been the object of this research to study these hitherto little known factors in relation to their bearing on commercial retorting.

A method has been devised for the determination of the amount of heat involved in the conversion to oil of the organic material in the shale, and the value has been determined on three quite different types of shale. It was found that these values for the three shales used ranged from 421 to 484 cal. per g. of oil and gas produced.

The heat conductivity of the shale has been determined for this work, and the coefficient of thermal conductivity has been found to be 0.00086, expressed in c. g. s. units.

The specific heat has been determined and found to be around 0.265 for most shales.

Part I of this paper† has shown that certain fundamental conceptions as to the manner in which the organic material decomposes are different from those ordinarily accepted. The hitherto generally accepted explanation of the manner in which these shales decompose is that, under the influence of heat, the organic material breaks down from a high-molecular-weight, insoluble substance to form petroleum-like hydrocarbons. These hydrocarbons increase in density and boiling point as the temperature rises, that is to say, the first product of destructive distillation of shale is the light hydrocarbon oil corresponding to gasoline in physical properties. The next is a somewhat heavier product like that found in the kerosene fractions, and the next still heavier, and so on until, finally, heavy residuents, such as fuel oil and paraffin, are produced. Part I has also shown that the organic material does not decompose as above outlined, but that its first product of decomposition is a heavy solid or semi-solid bitumen soluble in carbon bisulfide, whereas the original material was but very slightly soluble. The production of petroleum-like oils is, then, the result of the decomposition of these heavy bitumens by cracking.

The importance of this idea is that it places the production of oil, especially gasoline, from shales in the same category as the production of gasoline from the cracking of other oils. It should, therefore, promote the design of a shale retort along this line.

At the beginning of this work little or nothing was known as to the amount of heat required to convert to hydrocarbons the pyrobitumen of the shale. It was not even known whether the reaction was endothermic or exothermic, and, as this could easily be a factor of prime importance in the design of a retort, it was decided to determine it experimentally. The design of the apparatus and the method of determining this constant are described in this paper. Also, there have been included data on other heat factors, such as specific heat and heat of vaporization. Additional information can be obtained on these and other constants by consulting the original articles referred to.

HEAT FACTORS

In the design of a retort it is desirable to know the quantity

[1] Presented in part (together with Part I) before the New York Section of the American Chemical Society, New York, N. Y., January 7, 1921.

[2] A dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York, N. Y.

* Numbers refer to bibliography at the end of the paper.

† THIS JOURNAL, 13 (1921), 613

of heat that must be added to bring the shale to the distillation temperature, to cause a decomposition of the organic matter, and to distil off the products.

SPECIFIC HEAT—The specific heat will vary according to the composition of the shale. It could not be expected that the specific heat of all shales would be the same, when it is considered that the shales are mixtures of mineral constituents of varying proportions, through which an organic material is disseminated, also in varying proportions. The specific heats of certain shales are tabulated below.

SUBSTANCE	Specific Heat	° C. Temperature Range	AUTHORITY
DeBeque Shale	0.265	20–90	Bureau of Mines[4]
Parachute Shale	0.242	20–90	Bureau of Mines
DeBeque Shale	0.273	18–90	McKee and Lyder
DeBeque Shale	0.280	20–90	McKee and Lyder
(Shale Residue)	0.223	20–90	Bureau of Mines

In this work the method used was the simple method of mixtures as ordinarily applied. The average of the raw shale, which is probably as accurate as is necessary, is 0.265.

HEAT CONDUCTIVITY—The heat conductivity of the shale should be expected to vary with composition as does the specific heat. At our request, this constant was determined on four samples of Parachute shale by the Bureau of Standards at Washington, D. C. The method used was one that they have devised for the determination of the heat conductivity of poor conductors, such as asbestos board. It should be quite accurate. Briefly, the method consists of placing a slab of material in the side of a well insulated box, heated from the inside, and comparing the loss of heat, with the sample in place, with that of a sample of material of the same dimensions whose conductivity is known. The samples for the experiment were prepared by having a stonecutter saw them from a large lump of shale. They were cut 7 in. square and 0.75 in. thick. The slabs were so cut that in conducting heat from one face to the other the heat would pass perpendicular to the stratification of the shale. The coefficient of conductivity as determined on the samples was 0.00086 (c. g. s. units). This shows that the shale is four times as good a conductor as paraffin (0.0002), about one-third as good as glass (0.0025), and about one-sixth as good as marble (0.005).

This value is quite different from that obtained on other shales by the Bureau of Mines. Their value is 0.0038.[4]

HEAT OF VAPORIZATION—The heat of vaporization is a factor of considerable uncertainty. It has been shown that these shales decompose into a heavy tar-like substance and that the cracking of this product produces shale oil. The heat required to vaporize this heavy tar-like material must include the heat necessary to form shale oil from it. At present, little can be said as to this value; the best that can be done is to include the true heat of vaporization of similar oils. Gräfe has calculated these values for "Braunkohle" oils.[5] The following are his data:

MATERIAL	Average[1] Boiling Point ° C.	Sp. Gr.	Heat of Vaporization Cal.	Heat to Raise to B. P. Cal.	Total Heat Cal.
Light crude	216	0.883	86.5	82	168.5
Heavy crude	270	0.905	68.8	105	173.7
Paraffin oil	328	0.920	63.3	130	193.3
Heavy paraffin oil	346	0.933	53.8	138	191.8

[1] The average boiling point is the average value of the boiling ranges of all of the 5 per cent cuts of the oil.

The heat of vaporization of Russian petroleums is around 75 cal. per gram.[6] The specific heat of most petroleum oils may be taken as around 0.42.

HEAT OF REACTION—The heat of reaction is, in this case, the heat of decomposition of the kerogen of the shale into oil. Heats of decomposition are usually expressed as the number of calories absorbed or evolved per gram mole of the decomposing substance. In the present case, nothing is known of the molar weights involved, and it is therefore desirable to express the heat of reaction, *i. e.*, the heat of decomposition, either in terms of the number of calories per gram mole of shale decomposed, or, better, in terms of calories per gram of oil (and gas) formed. In this work the use of the heat of reaction, meaning the number of calories per gram of oil and gas formed, has some advantages; for instance, it permits, at once, the comparison of different shales irrespective of the amount of kerogen they contain.

Heat of Combustion Method—In determining the heat of reaction of organic compounds a common method is to determine the heat of combustion of the original material and of the products of the reaction. Hess, in 1840, showed that the amount of heat generated by a chemical reaction is the same whether it takes place in steps or all at once, it being only the initial and final states that count and not the path by which the reaction proceeds. If, then, a given organic substance is burned to carbon dioxide and water, and the heat involved in the reaction is determined by a calorimetric method, a certain value is obtained. If, on the other hand, the substance is changed by heat into one or more other substances, and the heat of combustion of these products is determined in the same manner as above, the difference in the heats of combustion will represent the heat that it took to go from the original substance to its decomposition product. In the case of a material like coal where the products can be collected and the heat of combustion of the original coal, as well as of all of its products of decomposition, determined, one is able to arrive at a value for the heat necessary to decompose the coal. Mahler did this in the case of some coals. In a substance like shale the experimental problem is somewhat difficult. The carbon compound or combustible material is relatively low, ranging from 10 to 50 per cent. This means an exceedingly high residue or ash. If these high residue materials are burned in an ordinary bomb calorimeter the combustion is nearly complete, and constant results are generally obtained; yet in every case the residue is a fused jet-black material in which unburned carbon is in evidence. In order to show the extent of this combustion, runs were made on a shale, and the residue from a bomb calorimeter was burned in a Fleming apparatus of the type ordinarily used for the determination of carbon in steel. The heat value of the shale and the corresponding correction for carbon is shown in the table. In making this calculation, it is assumed that all the organic material left in the ash is there as amorphous carbon and not as a hydrocarbon. This assumption seems fair, in view of the very high temperatures attained in the bomb.

Sample No	Heat of Combustion Cal. per Gram	Carbon in Residue	Correction Cal. per Gram	Correction Per cent
1	2949	0.0031	6.80	0.23
2	2954	0.0035	7.70	0.26
3	2963	0.0038	8.30	0.28
4	2941	0.0036	8.50	0.29

While this total correction is small on the original shales and, if made in the manner described, is, no doubt, accounted for to within the experimental error, when it comes to making the same correction on the residue of the shale after the oil has been distilled off, it becomes more significant.

Sample No.	Heat of Combustion Cal. per Gram	Carbon in Residue	Correction Cal. per Gram	Correction Per cent
1	1319	0.014	30.2	2.3
2	1318	0.016	35.1	2.5

Here there is an error of 2.5 per cent if left uncorrected, and one somewhat less if it is corrected. Any carbon dioxide remaining in the residue after combustion would appear by this determination as a corresponding amount of carbon, but no evidence of carbonates was found in the residue after it had been heated in a bomb calorimeter.

A further objection to the method as applied to the shale is that there is a large percentage error, owing to the small value of the heat of combustion of the residue after the oil has been distilled off. From the second table it is seen that only 1136 cal. per g. of shale are obtained; this may be in error by 2 per cent. Another disadvantage in this connection is that it is differences of heat which are being considered, and the differences are usually small, which correspondingly increases the percentage of error in the final result.

After making several preliminary runs by this method it was decided that the errors involved were too great and that it would be best to work up an apparatus in which the heat of reaction could be determined experimentally.

Euchéne Method—Euchéne,[7] in his calculations on "Thermo Reactions," has calculated the heat quantities involved in the decomposition of coal. This he did by summing up the heats used and those consumed in the commercial distillation, and striking a balance which showed that, in the ordinary coal-gas process, heat, though it may be small, is liberated. His method, which was somewhat tedious and subject to large error, was briefly as follows:

> First, he determined how much fuel it took to distil a given amount of coal, and the heat value of the fuel was calculated from its elemental composition. To this heat he added that which was recovered in the process from the formation of certain gases which are formed with a liberation of heat: carbon dioxide, carbon monoxide, methane, water, hydrogen sulfide, and ammonia are the ones involved. The sum of these two quantities would give him the total amount of heat available for the distillation of coal.
>
> The heat used in the process was then calculated by duly considering the heat used in the formation of such gases as ethylene, benzene, carbon bisulfide, and cyanogen, which are formed with the absorption of heat. To this was added the heat lost in the hot gases, coke, ash, and by radiation. By balancing up these quantities he found that the entire process liberated heat to the extent of from 12.39 to 63.51 cal. per g. in certain English coals.

This value may be considered to fall well within the very large experimental error of such intricate calculations, but the work of Mahler, referred to above, shows also that the heat of combustion of the original coal is greater than that of the products by some 254 cal. per g. This value, while not agreeing with those of Euchéne, is in the same direction and of the same order and shows that, taken as a whole, heat is liberated in the processes.

Qualitative—Some evidence as to the intricacy of the reaction may be gathered from the work of Hollings and Cobb[8] on coal. While their work was purely qualitative, it shows the procedure of such reactions. The method employed by these workers was to place in an ordinary combustion furnace two boats, side by side, one containing the coal to be distilled, and the other, a nonvolatile inert coal which would undergo no change as the distillation of the volatile coal proceeded. As the two were heated up together, the change in temperature was measured by means of placing in each the junction of a differential thermometer, such as is used in metallurgical work in determining the transition point. If the volatile coal absorbed or evolved heat and the other did not, their difference in temperature would be recorded by the instrument, but as long as both rose in temperature by simply heating up with the furnace, no abnormal deflections would be noticed in the recording instrument.

By this method they showed that coal went through several stages of decomposition, some being accompanied by exothermic and others by endothermic reactions.

Up to 410° C.	Reaction endothermic
410° to 470° C.	Reaction exothermic
470° to 610° C.	Reaction endothermic (CH_4 evolved)
610° to 800° C.	Reaction exothermic (H_2 evolved)

There is a definite similarity between these results and some which the present authors have obtained by an entirely different method. A small brass retort (see Part I, Fig. 2) containing the shale and a 1000° F. nitrogen-filled thermometer was placed in an electrically heated bath after the temperature of the bath had reached a rather high value (850° F.). The temperature of the bath was measured by means of a rare metal thermocouple, calibrated in terms of 1000° F. thermometer. As the temperature rose, oil was formed and distilled over, and, within about an hour, the entire 50 g. of shale could be decomposed. After the completion of the run on shale, a residue (the same shale from which the oil had been distilled) was run in the same manner, and the temperature effects in both runs were compared. The results of this experiment are graphically represented in Curves I and II, Fig. 1. The method used in plotting the data was to plot time in minutes as abscissa and the temperature changes as ordinate, and, in order to facilitate plotting, the ΔT was taken as the average for each 5 min. Reference to the curve shows that, with the shale in the retort, the temperature change remained constant until the still reached 745°, showing that no appreciable decomposition was taking place and that the still was simply rising in temperature with the bath. As the temperature increased, however, the temperature changes became smaller, passing to a negative value within the next 10 min. As the heating continued, the temperature change again approached normal and was followed by another drop. It then rose gradually to the end of the run. This is, of course, a rough measurement, but it indicates at least two distinct stages in the reaction. Attention is here called to the corresponding curve for the run on the residues. It will be noticed that the time required to reach approximately the same temperature (800° F.) in the case of the residue is only about half that in the case of the shale. About 4 g. of oil were obtained, and Curve I must be assumed to represent partly the latent heat of vaporization of this oil; but the large difference must be taken to mean that the heat of reaction over the whole range of the curve is endothermic, and that the rise at 764° is an indication of an exothermic reaction.

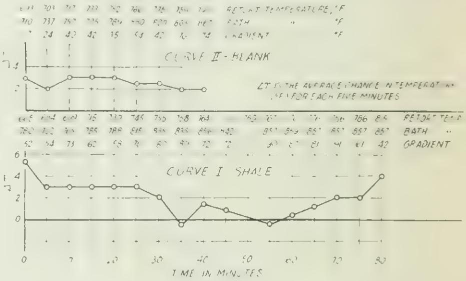


FIG. 1

DESIGN OF APPARATUS FOR MEASURING HEAT OF REACTION

Inasmuch as these data indicated a measurable heat of reaction, it was determined to design, if possible, an apparatus wherewith its value could be accurately measured. The factors entering into such a determination are as follows:

1—The heat conductivity of the material is very small (0.00086); therefore a considerable temperature gradient must be maintained to decompose a particle of shale at some distance from the source of heat.

2—Unless a very high temperature gradient is maintained the reaction will take place very slowly. (It extended over about an hour in the experiment above described.)

3—The product obtained depends in character upon the manner in which the shale has been decomposed.

The problem was, therefore, to design some sort of calorimeter in which a high temperature could be maintained while the shale was being decomposed, and one to which large amounts of heat could be added without abnormally high calorimeter temperatures being produced; that is, a temperature change of more than 10° C. was not advisable in the calorimeter, and accordingly the calorimeter should be so designed that the total heat added would not raise it more than this. The calorimeter should also be such that the radiation correction, due to the comparatively long time in which it must be run, could be calculated with a fair degree of accuracy.

DECOMPOSITION CHAMBER—The first problem undertaken was the design of a suitable decomposition chamber, and the points to be considered in this connection were (1) to be able to measure the heat energy added with sufficient accuracy, (2) so to design it that a high temperature could be maintained while the decomposition was going on and yet to eliminate conduction and waste heat to the surrounding water, (3) to arrange the apparatus to cool as quickly as possible after the reaction ceased and, thereby, decrease the radiation correction, and (4) to make the parts substantial and rugged enough to stand repeated determinations.

As regards the first requisite, it was decided to use the resistance of an electric current as the source of heat. At the beginning, the assumption was made that the heat of reaction would be relatively large and that it would be sufficiently accurate to measure the energy by means of an ordinary ammeter and voltmeter, and it was believed that the line current in the building was sufficiently steady for use. As work progressed it was found that the apparatus gave only 3 to 5 g. of oil, and that its heat of reaction was so small that more refined methods were necessary. The current had to be taken from sixteen Edison cells, and, in order to reduce further the error in the quantity of heat supplied, a copper voltameter was substituted for the ordinary ammeter, and the voltmeter, which was a Weston instrument, was calibrated* and corrected and read to 0.01 of a volt.

The decomposition chamber was a brass cylinder about 1.5 in. in diameter and about 2 in. long. It was fitted with a center tube sealed up through the bottom and extending nearly to the top. This center tube was to serve as a passage for the oil vapor to leave the retort, to be condensed and collected in a receptacle fitted to the bottom of the center tube. This chamber is shown as A in Fig. 2, with the condensation chamber C attached to the bottom. All joints were hard soldered so that the apparatus would stand any reasonable temperature. The lid, through which ran the electrical leads, was fastened on by means of a union joint.

HEATING ELEMENT—The heating element of the apparatus proved to be the most delicate part and, at first, required frequent renewal. Great difficulty was experienced in getting a properly insulated heating element so small and yet substantial enough to stand constant use. This was finally accomplished by winding a fine nichrome (22-gage) wire around an ordinary alundum extraction thimble and cementing it in place (the wires properly distanced from one another) by means of alundum cement. The resistance of this wire was so high that it was found best to wrap two wires and connect them in parallel. This permitted the use of fine wire, making possible ease of wrapping and even distribution, and at the same time sufficient current to effect decomposition.

In the first apparatus made, the coil was large enough just to fit within the walls of the retort, it being the intention to place all of the shale within the alundum thimble and to heat entirely from the outside. After many attempts this was given up because (1) more heat was given off to the walls of the retort than was utilized by the shale, and (2) the extremely low heat conductivity of the shale and the fact that it was all relatively far from the outside of the retort made cooling very slow. To avoid this a smaller heating element was made and placed in the center of the retort, and the shale to be decomposed was placed around it instead of in it, as in the previous case. This improvement, more than any other one thing, made possible the desired decomposition. First, it caused the shale, which is a splendid insulator, to act as its own insulation from the surroundings while the heating was going on, and, second, it placed the shale near the surface of the retort where effective cooling could be accomplished when it was desired to bring the retort to the temperature of the calorimeter.

CALORIMETER—With the retort thus designed and tested as to the amount of oil that could be recovered in a given length of time, etc., the next problem was to find a way to measure the heat recovered during the decomposition. Of course, an ordinary standard calorimeter would suggest itself as the most likely piece of apparatus to use, and it was thought that in this connection a gas calorimeter of the Junker type might be successful. The ordinary bomb type (Mahler, for instance) held only 2000 g. of water, and preliminary experiments showed that heat to the extent of 30,000 to 40,000 cal. would be necessary to effect sufficient decomposition to render measurements accurate. With 2000 g. of water, therefore, the final temperature would be from 15° to 20° C., which was entirely out of the question, but the gas calorimeter, being a constant flow apparatus, seemed to overcome this disadvantage. The method was to insert the decomposition chamber, fitted up as described, into the body of the calorimeter where the combustion ordinarily takes place, to close the bottom tightly and blow a steady current of air through, virtually creating an artificial product of combustion, and to measure in the ordinary way the heat given off to the water. This failed completely because the retort cooled so slowly in the current of air that about 100 lbs. of water had to be put through before the retort came to the temperature of the incoming water. With this large amount of water the small error due to temperature readings would be of the same order as the value of the heat of reaction sought.

The only objection to the use of the bomb type calorimeter was, as has been mentioned, the fact that it did not hold enough water, and it seemed that, if the bucket were removed from that type of apparatus (one of the Emmerson makes), the insulation of which is a large Dewar flask, and the flask simply filled with water, the capacity would be greatly increased and no serious disadvantage would be incurred. By this method 4000 g. of water could be used and by proper insulation, the retort could be heated and, at the proper time, quenched and cooled down at will.

INSULATION—In order to heat the retort effectively in a body of water it was necessary to insulate it very completely and to be able to quench it quickly when once the run was complete. To accomplish this an outside shell, also made of brass, was made large enough to fit over the retort and leave a 0.5-in. space for insulation. This space was loosely filled with woven asbestos cloth. The jacket was fitted with a screw cover with insulated lead wires through for carrying the current. The jacket was also fitted with a side tube, F in Fig. 2, connected at the top and bottom. In the bottom of this tube was placed a ball valve, and through the tube was fitted a plunger. The object of this arrangement was to allow the apparatus to heat up with the

---

* This instrument was calibrated by Dr. F. A. Strauss, to whom thanks is extended.

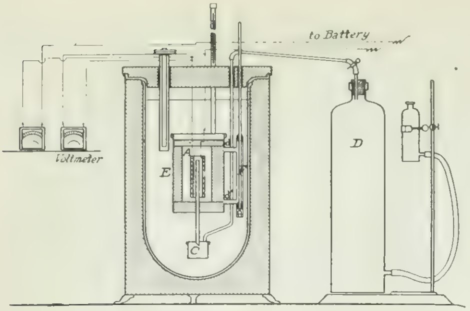


Fig. 2

insulating material dry and then, when the run was finished, to pump water from the calorimeter by means of the plunger, thus bringing the retort back to the temperature of the calorimeter as quickly as possible. This pumping arrangement worked very well.

The complete apparatus consisted of a brass retort A, Fig. 2, fitted with a water-tight cover and insulated plugs through which the electric lead wires were passed. It also had a center tube extending nearly to the top and 3 in. below the bottom of the retort. On the bottom of the center tube was a small brass receptacle fitted with a screw cover, and an outlet through which the permanent gases could escape.

A, the retort proper, was surrounded by a brass jacket large enough to permit the insulating material (asbestos cloth) to be placed between them and leave space for water to circulate. The outer shell or jacket was fitted with a side tube containing a hand-worked piston pump by means of which water was circulated through the apparatus to cool it down to the temperature of the calorimeter. The whole decomposition chamber was suspended from an especially made lid to the calorimeter.

Procedure

The procedure in making the run was as follows: The retort was filled with a weighed amount of shale, and, after all connections were made to prevent the water from getting into the decomposition chamber, the whole was suspended from the lid of the calorimeter, immersed in a weighed amount of water (4000 g.), the thermometer adjusted, and the stirrer started as in a bomb calorimeter determination. At the beginning of the determination the temperature of the water in the calorimeter should be about as much below room temperature as it will be above it when the run is finished. This decreases the radiation corrections. After the decomposition chamber and parts in contact with the water had come to the water temperature the current, which should be adjusted to about 7 or 8 amperes at 16 volts, was turned on. Half-minute readings were taken on the voltage and minute readings on the water temperature. At this rate of supplying heat the current may be left on about 23 min. without raising the temperature of the calorimeter more than 10° C. This will decompose shale sufficient to furnish 2 to 6 g. of oil and gas. At the expiration of this time, the current was turned off and water admitted by raising the pump plunger. Water was pumped through the apparatus continually as long as the temperature rose. The decomposition chamber was then removed, and the oil and water were removed from the distillation chamber C. The shale was taken out of the retort and extracted with benzene. This was necessary because the larger part of the oil had not distilled over, but remained in the shale as a tar-like substance. The gas collected in the bottle D was run into a Bunsen specific gravity bottle and its gravity determined. From its specific gravity and the volume, the weight of the gas may be determined.

Water Equivalent

On account of the variations in the kind of material used in making the parts of the calorimeter (glass as a container, brass for retort and jacket, alundum heating core, asbestos insulating material, nichrome resistance, and copper leads) it would have been difficult to calculate the water equivalent of the calorimeter from the specific heats of the parts. This was particularly true of the heat taken up by the glass containing vessel. It was a large double-walled vacuum flask holding 4000 g. of water, the whole being permanently fastened into the felt insulation of the calorimeter proper. The entire flask was, therefore, not heated to the temperature of the water, only the inner wall being in contact with it; hence there was no way of weighing the particular portion of the flask heated. The water equivalent could, however, be determined by methods similar to those used in the determination of the water equivalent of an ordinary bomb calorimeter. The method was to heat up the apparatus with all of its parts in place and under the conditions under which an actual run was made, excepting that instead of using the shale on which the heat of reaction was to be determined, a residue from a previous run which contained no volatile matter was placed in the decomposition chamber. Then, knowing the weight of the water present and the energy added, the water equivalent could be calculated. The calculations involved in determining the water equivalent were as follows:

Let H_1 = heat added during the process
V = volts (average at which current is supplied)
m = weight of copper deposited on electrode of voltameter
e = electrochemical equivalent of copper, 0.0003294
f = mechanical equivalent of heat in cal., 4.18

Then $$H_1 = \frac{(Vm)}{0.0003294 \times 4.18}$$

Also let H_2 = heat recovered by calorimeter
W = weight of water in g.
w = g. water equivalent of calorimeter
t_1 = initial temperature, temperature of calorimeter ° C. (corrected)
t_2 = final temperature of calorimeter ° C. (corrected)
M = weight of oil and gas recovered

Then $H_2 = (W + w)(t_2 - t_1)$

Water equivalent is then found by equating the values of H_1 and H_2 and solving for W

$$w = \frac{(Vm) - W\ (t_2 - t_1)\ 0.0003294 \times 4.18}{0.0003294 \times 4.18\ (t_2 - t_1)}$$

By this method w was found by two determinations to be 157 g. and 163 g., or an average of 160 g. The value of the weight of the water was taken to be 4000 + 160, or 4160 g.

Errors and Corrections

radiation losses—In the actual manipulation of the apparatus the time taken to heat the shale to its decomposition temperature and to transfer all of the excess heat to the calorimeter was considerable. On an average it was from 40 to 50 min. and, even though the apparatus was well insulated (by a vacuum jar) and the radiation per minute was relatively small, yet when the operation was extended over such a long time the radiation factor was quite large. It would amount to as much as 0.1° C. This would mean approximately 410 cal. on the total run. This correction could be largely eliminated by starting the experiment as far below room temperature as it would be above room temperature at the finish if the time were the same during which it remained above and below room temperature; but this is not the case. At the start, assuming that the system was 4° or 5° below room temperature, it would heat up with only the normal radiation from the room, but after the operation was finished with the temperature of the water some 4° or 5° above that of the room, the apparatus cools down at a rate which depends upon the rapidity with which the heat is transferred from the inside of the retort to the water. This is exceedingly slow and the instrument may run at a constant maximum temperature for as much as 6 or 7 min. Therefore, the calorimeter may remain at this high temperature for a considerable time.

In order further to eliminate the radiation losses, a correction was applied each time. The method adopted was the graphical one used by the Bureau of Standards in connection with their bomb calorimeters.[9] It is found to work out very well in the latter case, and, inasmuch as the operation is similar in principle to that applied here, the correction is probably the most applicable one to be had.

Let r_1 = Rate of rise (or fall) of temperature at start of experiment

r_2 = Rate of fall (or rise) of temperature at finish after all of heat has been dissipated to the water

t_1 = Time at which current was turned on

t_2 = Time at which temperature begins to fall after operation is complete

t_3 = Such a time that the total heat radiated to the calorimeter from the surroundings while it is below room temperature is exactly equal to that radiated to the room by the calorimeter when it is above room temperature. In other words, it is the time at which the calorimeter ceases to absorb heat and starts to radiate it. For graphical reasons it is taken to be 0.6 of the total rise of the calorimeter.

Then $r_1 \times (t_3 - t_1)$ Heat absorbed by the calorimeter and is, therefore, added to the initial temperature and heat radiated by the calorimeter to the surroundings

$r_2 \times (t_2 - t_3)$ This is added to the maximum temperature

It is seen that these two temperature corrections tend to equalize one another, and if the proper conditions, such as starting at the right temperature and running the proper length of time, could be established, they would cancel each other. A typical set of data on Colorado shale is included to illustrate the manner of this correction.

	Grams
Wt. of electrode	84.5260
Wt. of electrode + copper	87.2360
Wt. of copper deposited	2.7100

Time	Temp. ° F.	Volts	Amps.
3:44.30	64.9		
:45	64.98		
:46	64.99	12 00	
:47	65.00	12.00	6.49
		12.03	
:48	65.10	11.95	
		12.00	
:49	65.20	11.98	6.49
		12.10	
:50	65.35	11.95	
		12.00	
:51	65.55	12.00	7.05
		12.00	
:52	65.80	14.10	7.00
		14.05	
:53	66.05	14.00	
		14.00	
:54	66.40	14.00	
		14.00	
:55	66.70	14.00	7.05
		14.00	
:56	67.20	14.00	
		14.00	
:57	68.70	13.98	7 10
		14.00	
:58	69.00	14.00	
		14.00	
:59	69.60	13.00	
		13.00	
4:00	70.10	12.95	6 90
		12.75	
:01	70.60	12.90	
		12.95	
:02	71.20	13.05	7.00
		12.90	
:03	71.80	12.95	7 00
		13.00	
:04	72.25	Current off	Time 17 5 min.
		Av 13.08 volts	

DATA (Concluded)

Time	Temp. ° F.	Volts	Amps
:05	73.30		
:06	74.40		
:07	75.20		
:08	76.60		
:09			
:10	77.65		
:11	78.10		
:12	78.35		
:13	78.55		
:14	78.85		
:15	78.89		
:16	78.95		
:17	79.04		
:18	79.10		
:19	79.15		
:20	79.20		
:21	79.24		
:22	79.26		
:23	79.27		
:24	79.28		
:25	79.29		
:26	79.30		
:27	79.30		
:28	79.30		
:29	79.30		
:30	79.30		
:31	79.30		
:32	79.30		
:33	79.30		
:36	79.29		
:42	79.26		

	Ohms
Resistance of voltmeter	180.4
Resistance added	60.0
Total	240.4

$$\text{Voltage} = \frac{240.4 \times 13.08}{180.4} = 17.41$$

Weight of electrode = 2.7100 — 0.0271 = 2.6829

Initial temperature	64.99 ° F.
Stem correction	0.00
Calibration correction	—0.07
$r_1 (t_3 - t_1) = 0.01 \times 20 = 0.20°$	0.20
Corrected initial temperature	65.12
Final temperature	79.20
Stem correction	0.00
Calibration correction	—0.07
$r_2 (t_2 - t_3) = 0.005 \times 27 = 0.13$	0 13
Corrected final temperature	79.26

Thus it is seen that there is an actual correction of 0.20 — 0.13 = 0.07° F.

It will be noticed that the temperature reached a maximum and ran along constant for 8 min. The question might arise as to whether the time t_2 should be taken at the time when the temperature reached a maximum or at the end of the 8 min. It is probably advisable to take it at the end of the 8 min. because the retort is still radiating heat to the water, as otherwise the temperature would start to fall.

VOLTMETER RESISTANCE—Another correction became necessary because of the manner in which the determination was made. The voltmeter was kept in the circuit continuously instead of plugging it in when it was desired to make a reading. This was done because the readings were taken every half minute, and it was simpler not to throw the voltmeter out of the circuit between the readings. The resistance of the voltmeter was known, and the current it took could readily be calculated. This amounted to the equivalent of about 1 per cent of the weight of the copper deposited on the electrode. It was, therefore, subtracted each time.

The method was subject to several sources of error which could not be eliminated. These were calculated so far as possible.

ERRORS IN HEAT SUPPLIED—In the heat supplied the first error would be that due to voltage. The readings of the voltmeter were taken every half minute, and the average of these was the voltage used. The readings, when corrected by applying a standardization correction, should be quite accurate, but, unfortunately, the batteries used were not in first-class condition, and the voltage varied somewhat. The readings were made to 0.01 volt, which is approximately 1 in 1600. As a result of this variation, the average was probably not better than 0.02 volt, which is 0.13 per cent.

Table I

		Temperature ° F.																	
SHALE	Run No.	Initial	Total Correction	Corrected Initial	Final	Total Final Correction	Corrected Final	Rise ° C.	Heat Recovered Cal.	Volts	Weight of Electrode G	Heat Added Cal.	Wt. of Heavy Oil G.	Wt. of Light Oil G.	Wt. of Gas G.	Total Wt. G.	Difference of Heats	Heat of Reaction.Cal. per G.
Colorado	1	64.99	0.12	65.11	79.30	0.06	79.36	7.91	32905	17.70	2.693	34641	1.880	0.840	1.63	4.35	1730	398
Colorado	2	66.43	0.03	66.40	80.05	0.12	80.17	7.54	31366	16.90	2.703	33198	2.470	0.648	1.10	4.22	1832	434
Colorado	3	71.31	0.07	67.38	82.81	0.04	82.85	8.60	35776	16.74	3.065	37287	2.310	0.773	0.50	3.59	1542	430
Nevada	4	68.55	0.08	68.63	82.29	0.10	82.39	7.64	31782	16.62	2.707	32696	1.263	0.100	0.64	2.00	914	457
Nevada	5	67.52	0.11	67.63	82.94	0.04	82.98	8.53	35485	18.06	2.820	37012	1.065	0.385	1.78	3.22	1527	474
Canada	6	69.86	0.12	69.98	84.35	0.02	84.37	7.99	33238	16.56	2.480	34195	0.924	0.360	0.70	1.98	957	484

The second error is that due to the amperage. The use of a copper voltameter upon which 2.7 g. of copper is usually deposited renders the correction extremely low. With customary precautions in weighing, the weight could easily be determined to 3 in 10,000, or an error of 0.03 per cent.

Heat losses due to leads, conductivity of alundum, etc., would probably not exceed 0.05 per cent.

Adopting the principle that the most probable error is represented by the square root of the sum of the squares of the respective errors, the probable error would be 0.14 per cent. On 30,000 cal. produced this would be 42 cal.

THERMOMETER READING—As regards the measurement of the heat recovered by the calorimeter, the largest error is, perhaps, that of reading the thermometer. The thermometer used (calibrated Bureau of Standards, No. 10,482) was graduated to 0.05° F. Readings could be made to within 0.005° F. at initial and final temperatures, meaning that the error would not exceed 0.01° F. or 0.005° C. If the temperature rise was 70 (about the average), the error was 0.07 per cent.

It has been shown that after calculation for the radiation, the radiation correction is relatively small. There is no definite way of arriving at what the radiation error may be after calculation but it is certainly within 0.005° C. This would make a correction of 0.07 per cent.

The weighing of the water, evaporation losses etc., will not exceed 1.5 g., which on 4000 is equal to 0.03 per cent. Taking the square root of the sum of the squares it gives 0.10 per cent. On 30,000 cal. this would be 30 cal.

The maximum error due to subtraction of the heat recovered from the heat added equals 30 + 42 = 72 cal. This represents only the maximum actual error due to the subtraction of the heat. The actual value on the heat of reaction as finally obtained will be discussed later.

Table I is a summary of data and results.

The oil recovered was, for the most part, a heavy tar-like mass which was largely left in the retort mixed with the shale and had to be extracted with benzene. This is the character of the material produced during the first stage of decomposition from kerogen to shale oil. In order to produce lighter distillates, etc., from these it is necessary to crack these residua. The heat of reaction is then the heat necessary to change the kerogen into this primary product.

In determining the heat of reaction of these materials three quite different types of shale were used: (1) The Colorado shale which yields products similar in constitution to a mixed base petroleum oil such as is found in the Mid-continent field; (2) the Canadian shale which is more like an asphaltic base oil, such as California crude, and contains but little paraffin; (3) the Nevada shale which is peculiar in that it contains very large percentages of solid paraffin wax.

The average of the results of the Colorado shale is seen to be 421 cal. per g. of oil and gas produced, for the Nevada shale it is 465, and a single run on the Canadian shale shows 484. These results are, within the experimental error, practically the same, showing that this value is quite constant regardless of which shale is used.

SUMMARY—PARTS I AND II

1—An experimental method has been devised for the determination of the heat of reaction involved when these organic materials decompose to form oil and gas. This factor has been determined on three quite different shales and found to range from 421 to 484 cal. per g. of oil and gas produced. So far as is known, this is the first apparatus designed for the direct determination of this factor in shales or similar bituminous materials.

2—It has been generally thought that the organic matter in shales decomposed to form petroleum products as the primary products of decomposition. This research has shown that this is not the case, but that the primary product of decomposition is a heavy solid or semi-solid bitumen.

3—The decomposition temperature of the shale material has been shown to be quite definite and is within a range of 10° C. The decomposition takes place between 400° and 410° C.

4—When petroleum oils are formed from shales they are not formed directly from the pyrobituminous material in the shale, but they are formed by a cracking process from the semi-solid bitumen just mentioned. This cracking process is similar to the well-known phenomenon of the cracking of petroleum oils.

5—New data have been compiled on the heat conductivities of shale. The coefficient of conductivity was found to be 0.00086, expressed in c. g. s. units.

6—The experimental facts determined have shown that it will be possible to design a shale retort to be used simultaneously as a cracking still for shale bitumen and heavy residua from natural petroleum.

BIBLIOGRAPHY

1—Thomas Clarkson, "Facts About the Shale Oil Industry," *Oil and Gas J.*, **17** (1919), 60.

2—M. J. Gavin, H. H. Hill, and W. E. Perdew, "Notes on the Oil Shale Industry," Bureau of Mines *Bulletin* **1919**.

3—Greene, "Oil Shales."

4—M. J. Gavin and L. H. Sharp, "Some Physical and Chemical Data on Shales," *Oil and Gas J.*, **19** (1920), 86.

5—E. Gräfe, "The Heat of Vaporization of Petroleum Oils," *Petroleum*, **5** (1910), 569.

6—C. F. Mabery and A. H. Goldstein, "On the Specific Heat and Heats of Vaporization of Paraffin and Olefine Hydrocarbons," *Am. Chem. J.*, **28** (1902), 66.

7—Euchéne, *Trans. Internat. Gas Cong.*, Paris, **1910**.

8—Hollings and Cobb, *J. Chem. Soc.*, **107** (1915), 1106.

9—Bureau of Standards, *Scientific Paper* **230**, 229.

American Ceramic Society Meeting at St. Louis, Mo., in 1922

The Twenty-fourth Annual Meeting of the American Ceramic Society will be held in St. Louis, February 27 to March 2, 1922.

St. Louis is growing to greater importance as an industrial city every year. It is one of the largest centers for refractories and heavy clay products, while enameled ware, glass, and terra cotta are abundantly represented. A week of trips for the inspection of plants would be none too long.

The Hotel Statler will be the headquarters of the Society, and its facilities for the comfort of the meetings are unexcelled. Large rooms for divisional meetings, with a choice of ballrooms and banquet halls for the general sessions, will be available; while the luxury of the private rooms is too well known to need description.

The Rare Sugars: Their Purity and Tests[1]

By Carl Pfanstiehl and Robert S. Black

Special Chemicals Co., Highland Park, Illinois

Since the chief use[2] of the rare sugars at present is for differentiating microörganisms by means of fermentation reactions, the matter of developing standards and tests is a vital one to the bacteriologist. The microörganisms which it is desired to identify or differentiate either refuse to ferment or do ferment a special sugar, sometimes with the added indication of gas formed. Manifestly the presence of foreign sugars, the hindering actions of organic or inorganic impurities, certain pH concentrations, etc., are of the utmost significance to the scientist. While the development of standards and tests involves a long and arduous investigation requiring some years for its definitive completion, it is to be hoped that this attempt to formulate the requirements will assist others materially. Even this preliminary recommendation would not have been possible were it not for the helpful coöperation of many investigators in various research institutions whose interest has reflected the importance of this field of investigation.

In the first place, the standards for the sugars cannot be judged by the standards of reagent chemicals. For example, there is no chemical means which will detect 0.05 per cent of glucose in lactose (whose similar rotations, +52.5°, make it impossible for the polariscope to be of assistance), whereas *B. typhosus* will give this indication by a fermentation reaction. In fact, in differentiating the rare sugars, chemical method often has to give way to the delicacy of the polariscope or the selective action of yeasts and bacteria. Hence the tests for the purity of the rare sugars involve an extended and more difficult technique.

Standards of Purity

It is difficult to come to the practical conclusion of when a sugar is pure enough. Manifestly, since repeated purifications are costly, the standard should be no more exacting than the bacteriologist requires, and yet in the present state of the bacteriologist's knowledge he is scarcely ready to state that any particular limits of impurities are admissible. Nevertheless, certain standards are gradually being evolved, and it has been our aim to develop these toward a goal similar to Murray's "Standards and Tests for Reagent Chemicals." While the bacteriologists themselves must decide what shall finally be required, those who manufacture the sugars can contribute information as to certain very high standards which are readily attainable through careful manufacture. In order for the manufacturer to produce sugars of the required purity for reliable bacteriological results, he must work side by side with the bacteriologist and ever strive to meet the severest demands of the scientist's minute and fastidious "bugs." It is even believed that some of these organisms, the filterable viruses, may be not much larger than the molecule of sugar and may seriously consider the actual shape of the molecule in their decision as to whether or not they shall use it.

FREEDOM FROM OTHER CARBOHYDRATES—To begin with, the most important requisite of purity is naturally that the specific sugar be free from all other carbohydrates. The carbohydrates which may potentially be present should be known. The well-known chemical means for detecting foreign sugars present in a nonreducing sugar is Fehling solution. By this means nonreducing carbohydrates, such as the sugar alcohols and starches, can readily be shown free from, or contaminated with, reducing sugars. (Here it may be well to add the caution that Fehling solution, when boiled for a sufficient time with either sucrose or inulin, will hydrolyze it and indicate reducing sugars when none were originally present.) This chemical method is very evidently limited in its application. The most important means of detecting foreign sugars is the polariscope. If their presence is not detectable by rotation, we must turn to fermentation reactions. With the variable-sensibility polariscope, the use and accuracy of this instrument has been greatly extended, eliminating dependence on certain fermentation reactions formerly necessary.

HEAVY METALS—The test for heavy metals is important, since certain heavy metals will inhibit the action of certain bacteria. It is interesting to note here that distilled water drawn through a copper faucet has been known to inhibit the growth of certain organisms.

ALUMINIUM AND CALCIUM—Aluminium and certain calcium compounds will cloud the solution, upon whose clarity and brilliance the bacteriologist depends in making observations. The intensity of turbidity is an index to the amount of growth.

H-ION CONCENTRATION—The pH concentration is important within limits, since alkali destroys or transforms the carbohydrate or transforms it to another by molecular rearrangement, and 0.1 per cent of a free mineral acid will kill bacteria, a smaller per cent of course retarding their growth.

CHLORIDES AND SULFATES—Chlorides and sulfates, the bacteriologists believe, may be present in small amounts without deleterious effect upon fermentation reactions, but a high standard is recommended. A high standard offers greater accuracy for calculation and analysis, and at this stage of knowledge it is better to maintain the highest possible standard in every particular. For example, neutral salts, which will not interfere with growth of bacteria, are objectionable since they will cause disaccharides to be hydrolyzed when the solution is sterilized. Ash usually indicates sulfates, chlorides, calcium, aluminium, or heavy metals, or nonvolatile impurities, and must be kept extremely low.

MOISTURE—While moisture is not harmful in itself, it is practicable, from the manufacturing point of view, to keep this to a small fraction of 1 per cent. The low moisture content makes for accuracy in calculation and rotation and in the preparation of the sugar solutions by the bacteriologist. It is well known that certain sugars will deteriorate if moisture is present.

COLOR—The color of the sugars will be pure white unless foreign matter is present to an objectionable degree. Organic coloring matter interferes with the brilliancy of the solution and the detection of delicate color reactions.

MELTING POINTS—The melting points of the sugars are not to be relied upon as a test of purity, except in the case of the sugar alcohols.

General Tests for Purity Applicable to All Sugars

The general tests suggested for all the sugars, based on continuous experience, will first be given, and then the specific data for the sugars in order, as rotation, other sugars liable to be present, etc.

HEAVY METALS—Dissolve 1 g. in 20 cc. of distilled water. Should not give a precipitate or change color with hydrogen sulfide solution.

CALCIUM AND ALUMINIUM—Make a 10 per cent solution faintly ammoniacal, add a few cc. of ammonium oxalate solution. No precipitate should form.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] The use and possibilities of the sugars are described by Edmund H. Eitel, This Journal, **12** (1920), 1202.

SULFATES—Dissolve 1 g. in 10 cc. of distilled water, add a drop or two of hydrochloric acid, followed by a few cc. of barium chloride solution. No turbidity.

CHLORIDES—Dissolve 1 g. in 10 cc. of distilled water, acidify with nitric acid, followed by silver nitrate. At most a faint opalescence.

ACIDITY—Dissolve in distilled water. Should be neutral to methyl red.

ALCOHOL—Dissolve 1 g. in 5 cc. of distilled water, add 1 cc. of potassium hydroxide solution, and 1 cc. iodine test solution, warm to 60°. Should give no more iodoform than a blank.

A positive reaction does not prove the presence of ethyl alcohol, since many other compounds such as acetone, aldehydes, and the propyl and butyl alcohols, also give it. The determination and identification of small amounts of alcohol have been studied by Bacon[1] with special reference to its application in demonstrating alcoholic fermentation in food products. The weak alcoholic solution is three-fourths saturated with sodium chloride, and distilled. The saturation and distillation are repeated and the alcohol is then determined by refractometer or density method. Bacon recovered 96 per cent of a 0.100 per cent solution.

ASH—(Given under the specific carbohydrates following. Should be as low as practicable.)

MOISTURE—(Same as with ash.)

SOLUBILITY—All the carbohydrates except the starches should be completely soluble in water and give a perfectly clear and brilliant solution. The starches, inulin and glycogen, should be completely soluble in an excess of hot water.

ROTATION—A caution must be observed with sugars which contain free aldehyde or ketone groups, since the phenomenon of mutarotation is observed with them. Time must be given for rotation to become constant.

SPECIFIC TESTS

l-ARABINOSE:

Aldopentose, $C_5H_{10}O_5$

Specific rotation $[\alpha]_D^{20}$	+ 104.6° (9.73 g. per 100 cc.)
Ash	0.10 per cent
Moisture	0.10 per cent

Free from glucose: Determined by accurate rotation

DULCITOL:

Hexahydric alcohol, $C_6H_{14}O_6$

M. p.	188°
Ash	0.05 per cent
Moisture	0.10 per cent

Free from reducing sugars: Test with Fehling solution

ERYTHRITOL:

Tetrahydric alcohol, $C_4H_{10}O$

M. p.	126°
Ash	0.10 per cent
Moisture	0.10 per cent

Free from reducing sugars

d-GALACTOSE:

Aldohexose, $C_6H_{12}O_6$

Specific rotation $[\alpha]_D^{20}$	+ 80.3° (10.000 g. per 100 cc.)
Ash	0.05 per cent
Moisture	0.10 per cent

Free from glucose and lactose: Determined by accurate rotation

d GLUCOSE (DEXTROSE) ANHYDROUS:

Aldohexose, $C_6H_{12}O_6$

Specific rotation $[\alpha]_D^{20}$	+ 52.5° (9.097 g. per 100 cc.)
Ash	0.05 per cent
Moisture	0.10 per cent

Free from dextrin, maltose, etc.: Determined by accurate rotation. Free acid: A solution of 5 g. in 15 cc. of distilled water, mixed with 5 drops of phenolphthalein T. S., requires not more than 0.6 cc. of 0.1*N* potassium hydroxide V. S. to produce a pink color. (The use of *d*-glucose (dextrose) anhydrous for intravenous injection has made advisable the inclusion of this special test from U. S. P. IX.)

GLYCOGEN:

Polysaccharide, $6(C_6H_{10}O_5) + H_2O$, or multiple thereof

Ash	0.10 per cent
Moisture	0.10 per cent

Free from reducing sugars

INOSITOL:

Hexoxyhexamethylene, $C_6H_6(OH)_6$

M. p.	224°
Ash	0.10 per cent
Moisture	0.10 per cent

INULIN:[1]

Polysaccharide, $6(C_6H_{10}O_5) + H_2O$, or multiple thereof

Specific rotation $[\alpha]_D^{20}$	—38° (Average)
Ash	0.10 per cent
Moisture	0.10 per cent

Free from levulose: Since inulin will hydrolyze to levulose with boiling, any reduction tests involving boiling or the use of strong alkalies, as in Fehling solution, is apt to be misleading. Alkalies or acid salts will hasten the hydrolysis. The inulin solution in media should not be sterilized in the Arnold, though a purely inulin solution may be sterilized in the autoclave if made up with distilled water. This inulin solution can then be added to the media with a sterilized pipet as required. The bacteriological test of inulin for purity is more sensitive than any chemical test. Inulin should show no acid or gas production with *B. paratyphosus B.* or *B. proteus.*

C. S. Mudge[2] has found that it is not so much a question of intensity of heat as it is the length of time which the carbohydrate is exposed to the heat. A 10 per cent solution of a sugar can be sterilized in the autoclave, if made up with distilled water, while it may not be possible to sterilize a 0.5 per cent solution of the same sugar, in media, in the Arnold. This is probably due to small traces of acids and also salts in the media. Whenever there is danger of hydrolysis, the media and a 10 per cent solution of the carbohydrate should be sterilized separately. The sugar can then be added to each tube with a sterilized pipet, 0.5 per cent or 1 per cent as required. The above technique should be used in testing the inulin.

Make up a 10 per cent solution of the inulin by pouring 50 cc. of boiling distilled water on 5 g. of inulin. Sterilize at 100° C. for 15 min.

Sugar-free broth (free from muscle sugar by fermentation with *B. coli*) must be used, titrated to pH 7.6. Add 0.5 cc. of a 0.02 per cent solution of phenol red (phenolsulfonephthalein and 0.5 cc. of a 0.02 per cent solution of bromocresol purple (dibromo-*o*-cresolsulfonephthalein). Pour into fermentation tubes and sterilize. Three cc. of the sterilized inulin solution are added to the broth in a sterile manner. Mix and inoculate with *B. paratyphoid B.* Examine tubes after 24 hrs., 48 hrs., and one week for

(1) Acidity as indicated by change in color of indicator. (H-ion concentration may be determined by the Clark and Lubs method.)

(2) Gas production. Uninoculated controls are to be kept at incubator temperature at same time.[3]

Inulin free from reducing sugars should not show acid production and of course no gas. The rotation of inulin has not been accurately determined, different investigators reporting rotations varying in range 10°.[4] A 10 per cent solution of high grade inulin made from dahlias should have a specific rotation of not less than —35°.

The production of reducing sugars in inulin by boiling seems to depend upon the condition of the original substance from which the inulin is taken. The inulin in dahlias dug in the fall begins immediately to change over into compounds analogous to the long series of dextrins intermediate between starch and glucose. On boiling, these compounds, or at least some of them, especially in the presence of salts from the juice and traces of organic acids found in the juice, will hydrolyze to levulose. Therefore, boiling inulin, especially with Fehling solution, can give reducing sugars. The only reliable method for testing the reducing sugar in inulin therefore is bacteriological.

LACTOSE:

Disaccharide, $C_{12}H_{22}O_{11}$

Specific rotation $[\alpha]_D^{20}$	+52.42° (2.000 g. per 100 cc.)
Ash	0.05 per cent
Moisture	0.15 per cent

Free from glucose: Detect by acid production (and if present in sufficient amount by gas production) with *B. typhosus* or *paratyphosus B.* *B. proteus* may be used in preference to the two foregoing as it is nonpathogenic and easy to obtain

Free from spores: Make a solution, sterilize under ordinary precautions, incubate 48 hrs. No bacterial growth should result

d-LEVULOSE:

Ketohexose, $C_6H_{12}O_6$

Specific rotation $[\alpha]_D^{20}$	— 92.3° (10.000 g. per 100 cc.)
Ash	0.10 per cent
Moisture	0.10 per cent

The standard here given is more particular than the standard of Kiliani, *Ann.*, **205** (1880), 147.

---

[1] U. S. Department of Agriculture, Bureau of Chemistry, *Circular* **74**.

[2] *J. Bact.*, **2** (1917), 403

[3] This technique is from an excellent article by Masucci and Ewe. *J. Lab. Clin. Med.*, **9** (1920), 609

[4] Arthur J. Dean, *Am. Chem. J.*, **32** (1904).

Free from glucose: Determine by accurate rotation. Levulose when made from inulin should be uncontaminated with glucose; when made from invert sugar, glucose is removed only with the greatest difficulty

MALTOSE (HYDRATE):

Disaccharide, $C_{12}H_{22}O_{11} + H_2O$

Specific rotation $[\alpha]^{20}_{D}$	+131° (26 g. per 100 cc.)
Ash	0.05 per cent
Moisture	0.15 per cent

Free from dextrin: Determine by accurate rotation. Free from glucose: Test with Barfoed's solution, which is not reduced to any extent by maltose

d-MANNITOL

Hexahydric alcohol, $C_6H_{14}O_6$

Specific rotation (with borax) $[\alpha]^{20}_{D}$	+22.5° (10 g. mannitol+12.8 borax per 100 cc)
M. p.	166 5°
Ash	0.05 per cent
Moisture	0.10 per cent

Free from reducing sugars

d-MANNOSE·

Aldohexose, $C_6H_{12}O_6$

Specific rotation $[\alpha]^{20}_{D}$	+14.25° (10.000 g. per 100 cc.)
Ash	0.05 per cent
Moisture	0.10 per cent

PERSEITOL:

Heptahydric alcohol, $C_7H_{16}O_7$

Rotation (0.4 g. substance in 5 cc. saturated borax solution in a 1-dm. tube) $[\alpha]^{20}_{D}$	+ 0.39°
M. p.	188° C.
Ash	0.10 per cent
Moisture	0.10 per cent

RAFFINOSE (HYDRATE):

Trisaccharide, $C_{18}H_{32}O_{16} + 5H_2O$

Specific rotation $[\alpha]^{20}_{D}$	+104.5° (26.00 g. per 100 cc.)
Ash	0.10 per cent
Moisture	0.15 per cent

RHAMNOSE (HYDRATE):

Methyl pentose, $C_6H_{12}O_5 + H_2O$

Specific rotation $[\alpha]^{20}_{D}$	+8.37° (6.948 g. per 100 cc.)
Ash	0.05 per cent
Moisture	0.10 per cent

SORBITOL:

Hexahydric alcohol, $C_6H_{14}O_6$

M. p. (1 molecule H_2O)	55°
(0 5 molecule H_2O)	75°
(anhydrous)	110°
Ash	0.05 per cent
Moisture	0.15 per cent

Free from reducing sugars

SUCROSE:

Disaccharide, $C_{12}O_{22}O_{11}$

Specific rotation $[\alpha]^{20}_{D}$	+66.5° (4.275 g. per 100 cc)
Ash	0.05 per cent
Moisture	0.05 per cent

Free from reducing sugars

XYLOSE:

Aldopentose, $C_5H_{10}O_5$ (called by Fischer *l*-xylose, more properly *d*-xylose)

Specific rotation $[\alpha]^{20}_{D}$	+18.5° (10.239 g. per 100 cc.)
Ash	0.05 per cent
Moisture	0.10 per cent

The Standardization of Rare Sugars[1]

By Howard T. Graber

RESEARCH LABORATORY, DIGESTIVE FERMENTS CO., DETROIT, MICHIGAN

It is not the object of this paper to present anything new in discussing the standardization of sugars, but rather to apply our present knowledge and arrange it as a systematic procedure.

ROUTINE ANALYTICAL PROCEDURE

In the routine examination of all sugars in this laboratory, particular attention is paid to sampling to insure the selection of a sample representative of the whole lot. Since all of the rare sugars are made in relatively small quantities and receive a very thorough mixing after coming from the vacuum driers, sampling is not a difficult procedure.

The properly labeled samples are brought to the laboratory in 1-oz., amber, salt-mouth bottles, tightly stoppered with a paraffined cork. The labels bear the name, date of manufacture, and Rx. number, and a 3 × 5 index card accompanies the sample, which passes to the filing clerk who registers it in the record book kept for that purpose, the necessary assays to be made are placed on the card, and the sample and card then go to the chemist who makes the assays.

The routine analysis comprises a determination of specific rotation, color of the powder, moisture, ash, and solubility, as well as a determination of the presence of alcohol, chlorides, sulfates, calcium, barium, and heavy metals, and finally the reaction to the three indicators—litmus, methyl red, and phenolphthalein.

SOLUBILITY—In making the solubility test, a 30 per cent solution of the sugar in recently boiled and cooled neutral distilled water is used for sucrose, lactose, and dextrose, and comparison is always made with a standard dextrose of extreme purity. In this solubility test a notation is made of:

1—The color of the solution, which must be water-white.

2—The clearness, which must be brilliant without the slightest trace of haze.

3—The absence of foreign matter.

For the rarer sugars, a 10 per cent solution is used as above.

SPECIFIC ROTATION—For the saccharimetric readings, we use the Schmidt and Haensch half-shade saccharimeter bearing the certificate of the Bureau of Standards. The rays of white light, supplied by an incandescent light with etched bulb, are filtered through a dichromate absorption cell[1], with an inner separation of the glass plate walls of 15 mm., and filled with a 6 per cent solution of $K_2Cr_2O_7$. In designing the laboratory for polarimetric measurements, as well as in choosing the necessary apparatus, the specifications given on pages 122 and 123 of Bureau of Standards *Circular* **44** were followed. All measurements are taken at a temperature of 20° C. In all cases the measurements must be that of the accepted constant for the sugar at hand.

The actually determined saccharimetric normal weight of sucrose[2] and dextrose,[3] together with the calculated normal weights of lactose, maltose, raffinose,[4] fructose and invert sugar, as determined by the Bureau of Standards, are adopted.

In the case of those sugars which show mutarotation we prefer to let the solution stand over night at room temperature to come to equilibrium, rather than to add alkali.

COLOR—In the estimation of color, comparison is always made with a highly refined sample of pure white dextrose which reads 100 Red, 95 Green, 93 Blue-Violet, on the Palo tintometer. The standard and unknown are placed side by side on a piece of plate glass, blackened on the under side with lampblack and shellac. By this means, any difference of color in the two sugars is readily detected. In cases of doubt, the sugar under examination is also read on the tintometer.

ASH—The ash is determined in fused quartz dishes. Five grams of the sugar are weighed into a previously tared quartz dish, heated carefully over a low flame until the mass is charred and ceases to froth, and then placed in a muffle furnace, the muffle of which is quartz. The heat is evenly distributed over the bottom of the muffle by means of Fisher burners. A thermocouple, protected by a vitreosil shell, rests on the bottom of the muffle, and connects with a Brown recording pyrometer. The temperature of the muffle is held at dull red heat, or between 1100° to 1200° F., for 2 hrs. The amount of sugar taken for the determination of ash is always uniform, and by means of the above equipment the temperature and time of ashing are accurately controlled. The attempt is made to have our sugars as near ashless as it is possible to make them.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29 1921.

[1] Bureau of Standards, *Circular* **44**, 29.

[2] *Ibid.*, *Scientific Paper* **268**.

[3] *Ibid.*, **293**.

[4] *Ibid.*, *Circular* **44**, 81.

MOISTURE—The moisture determinations of these rare sugars are not entirely satisfactory, on account of four factors:

1—The hygroscopicity of some of the sugars.

2—The retention of water by occlusion, especially when crystallized in large grains.

3—The extreme sensitiveness of a few of the sugars to decomposition at temperatures much below 100° C., notably levulose and rhamnose.

4—The fact that such sugars as maltose, lactose, and raffinose retain variable amounts of water of crystallization under different conditions of drying.

On this account, whether the drying is to be accomplished under vacuum or in the open, each sugar must be considered by itself.

Five grams of the sugar are accurately weighed in a tared aluminium dish, approximately 55 mm. in diameter and 15 mm. high, fitted with an airtight cover of the same material. The sugar and dish are placed in an electrically controlled drying oven and held for 1 hr. at about 50° C. with proper ventilation to carry off the moisture. After this preliminary drying the door of the oven is closed, the temperature adjusted to 100° C., and the drying continued for an additional 4 hrs., or over night.

When the sugar is to be removed from the oven it is securely covered and transferred to the desiccator, cooled and weighed as usual, replaced in the oven, dried an additional 2 hrs., weighed again, and this method is continued until the weight is constant. In the case of levulose (m. p. 95° C.) and rhamnose (m. p. 92.8° C.) the sugar must be dried over night to constant weight at about 5° below the melting point.

In this laboratory, sugars are dried in large vacuum shelf dryers for 12 to 18 hrs., with a vacuum of 29 in. and running water with thermostatic control at not over 120° F. We attempt to make the residual moisture nil.

In the drying of invert sugar sirup and similar products, the usual technique of drying upon washed and ignited quartz sand is observed. Five grams of the sirup are weighed accurately, diluted to 250 cc. in a volumetric flask, and 50 cc. of this dilution taken from the moisture assay.

IMPURITIES—In testing for impurities, the procedure is as follows:

Alcohol—When 1 cc. of iodine T. S. and 1 cc. of potassium hydroxide T. S. are added to 5 cc. of a 20 per cent solution of the sugar in distilled water, no odor of iodoform should be perceptible after shaking.

Chlorides—When 3 drops of dilute nitric acid and 10 drops of silver nitrate T. S. are added to 5 cc. of a 10 per cent solution of the sugar in distilled water, and the mixture allowed to stand after shaking, the sugar should show not more than a very slight trace of chloride.

Sulfates—When 3 drops of dilute hydrochloric acid and 10 drops of barium chloride T. S. are added to 5 cc. of a 10 per cent solution of the sugar in distilled water, the sugar should show not more than a very slight trace of sulfates.

Calcium—When to the above solution, made alkaline with ammonium hydroxide, ammonium oxalate T. S. is added, no haziness or turbidity should develop.

Heavy Metals—When 2 cc. of hydrogen sulfide T. S. are added to 5 cc. of a 10 per cent solution of the sugar, and the mixture heated, no discoloration results. Also when 1 g. of hops is added to 160 cc. of a 10 per cent boiling solution of the sugar and the mixture boiled for 20 min., no greenish or black color, due to iron tannate, should be formed.

REACTION—In testing the reaction of our sugars, 4 g. of the sugar are dissolved in 50 cc. of distilled water, 2 drops of phenolphthalein are added, and 1 drop of 0.1 *N* sodium hydroxide must change the color of the indicator, showing the absence of excess acidity.

SPECIAL TESTS

The above tests are made on all sugars. In addition there are a few special cases to be considered.

GALACTOSE—In the routine analysis of galactose, we test for the presence of barium in 5 cc. of a 10 per cent solution of the sugar.

INVERT SUGAR SIRUP—In invert sugar sirup, the determination of reducing sugars is made[1] by the Defren-O'Sullivan method and it shows complete conversion on the dry basis. Nonreducing sugars are absent.

LACTOSE—In the analysis of lactose the sugar must be free from nitrogen and fat.

It must further show purity from dextrose by two separate tests:

1—Lack of acidity in culture media, under the influence of the *B. typhosus*.

2—Lack of gas formation in 96 hrs.' incubation of 10 cc. of a 20 per cent solution of the sugar in the presence of an excess of yeast.

RAFFINOSE AND RHAMNOSE—Ranffiose (5 H_2O) and rhamnose (1 H_2O) are put on the market as hydrates. Raffinose is also marketed as the anhydride.

SUCROSE—Sucrose is tested very carefully for reducing substances, according to the Bureau of Standards test,[2] with Striegler's solution. Under the condition of this test, if 10 g. of sucrose in 50 cc. of distilled water are added to 50 cc. of Striegler's solution (which has been boiled 1 min.) and the mixture boiled exactly 5 min., not more than 0.007 g. Cu_2O are precipitated. Immediately after 5 min. of boiling any possible further hydrolysis of the sucrose is eliminated by diluting the mixture with 100 cc. of cold, recently boiled, distilled water.

CONCLUSION

In conclusion it should be stated that in our work on standardizing these products, we aim at an ultimate degree of purity that will warrant the designation of "C. P." In our opinion, however, this designation should be reserved for chemicals in which present methods of analysis will reveal no traces of impurities. We cannot pretend that these rare sugars are susceptible of this perfection except by such repetitions of crystallization that the yield is absurdly small, and the resulting cost prohibitive. Therefore we refrain from using the term C. P., although constantly striving for it. In the present uses of these products, the main consideration is that each one shall be free from other carbohydrates. This we are able to achieve with an encouraging amount of success.

If research should now be directed to finding new uses for the so-called rare sugars, especially of commercial or less purified grade, it would be a great help to the development of the C. P. line, salable at a price that is reasonable.

---

[1] Leach, "Food Inspection and Analysis," 594.

[2] Bureau of Standards, *Scientific Paper* **268**, 80.

Soy-Bean Oil: Factors Which Influence Its Production and Composition[1,2]

By Carl R. Fellers

National Canners Association, 1613 L. C. Smith Bldg., Seattle, Washington

Physical and Chemical Properties

Soy-bean oil is more like linseed than most oils. In chemical properties however it is not unlike corn oil, but if it is to be used for paint manufacture special driers are desirable.[3] A tungate drier, such as a mixture of precipitated lead and manganese salt of tung oil, is excellent. A hard, dry, resistant film is produced with 5 to 7 per cent of drier, in 24 hrs. Soy-bean oil contains about 95 per cent of glycerol esters of fatty acids in proportion as follows: palmitic, 15 per cent; oleic, 56 per cent; linolic, 19 per cent; and linolenic, 5 per cent. It is to the latter three *unsaturated* acids that the oil owes its drying power. After hydrogenation, soy-bean oil can replace linseed in the manufacture of hard soaps. As an average of sixteen determinations, the iodine number of sixteen samples of imported and domestic oils was 129.2. The range was from 120 to 135. Soy-bean oil decreases the iodine number of linseed oil when mixed with it, but not appreciably until approximately 20 per cent of the former has been added.[4,5]

The results of tests made on soy-bean oil are given in Table I. There was considerable variation in color and appearance of the samples used for this work. The imported samples were composites of equal quantities of each of three distinct lots. The prepared samples were obtained by crushing and extracting with ether four different lots of each of the varieties being tested. Official methods were abandoned in several determinations because of the greater simplicity of Thompson and Morgan's[6] methods.

Table I

Source of Sample	Sp. Gr.	Refractive Index 25° C.	Iodine Number	Saponification Number	Acid Number	Drying Power
Varnish Co. No. 1	0.924	1.4748	130.1	194.6	0.8	Fair
Varnish Co. No. 2	0.923	1.4750	128.2	195.8	2.1	Fair
Varnish Co. No. 3	0.922	1.4736	131.3	190.2	0.3	Poor
Varnish Co. No. 4	0.925	1.4740	125.7	191.3	2.6	Poor
Med. Greeen Soy beans	0.925	1.4739	123.2	193.8	0.3	Poor
Black Eyebrow Soy beans	0.924	1.4726	125.0	195.0	0.2	Good
Ito San Soy beans	0.925	1.4732	128.1	193.5	0.17	Fair
Hollybrook Soy beans	0.924	1.4740	128.1	191.8	0.3	Good
Early Brown Soy beans	0.926	1.4720	128.0	193.0	0.2	Fair
Tarheel Soy beans	0.926	1.4741	132.3	193.0	0.55	Poor

Additional determinations were made upon two samples, particularly for the purpose of comparing imported Manchurian oil with domestic oil.

Table II

Source of Sample	Reichert-Meissl No.	Hehner No.	Neutralization Value	Unsaturated Fatty Acids	Saturated Fatty Acids	Ether No.
Varnish Co. No. 2	4.3	94.3	190.3	85.7	8.6	190.1
Imported Black Eyebrow Soy Bean (Composite of 16 Samples	5.2	93.0	195.2	84.9	9.2	187.2

These data show the close similarity which exists among different lots of soy-bean oil. The specific gravity is practically constant at 0.925 and the refractive index varies but little from 1.474. The iodine number is more variable, ranging from 123.2 to 132.3. Some investigators have maintained that imported oils have a higher value and hence better drying properties than domestic oils, but these data do not bear out this contention. Nemzek[1] points out that iodine value and drying power do not necessarily go hand in hand, although such is often the case.

The saponification values are fairly constant between 190 and 195, a value which is near the average for neutral oils. This high number also indicates that the percentage of volatile acids is not high and that there is but little unsaponifiable matter. This is of great importance to the soap manufacturer. The acid value varies considerably in the several samples. Two high values were found in imported oils. Gardner,[2] in his repainting tests at Washington, D. C., showed that the acid value of a sample of soy-bean oil increased in 2.5 yrs. from 3.8 to 5.7. The drying power of the oils was determined by exposing oil films of uniform thickness on pine boards. This was merely to enable the writer to class the oils roughly as good, fair, or poor driers. Sample 4 imported oil, and Tarheel and Medium Green oils were markedly poorer than the rest. In the former, the iodine value is low and the acid value is high. The low Reichert-Meissl number shows but a very small percentage of volatile fatty acids to be present. The percentage of insoluble fatty acids plus the unsaponifiable matter gives the Hehner value of an oil. As Thompson and Morgan[3] point out, this is a difficult determination to perform with soy-bean oil, since a solid cake of the fatty acids is hard to secure. Each result in Table II represents the average of four determinations. Since the per cent of unsaponifiable matter is so slight, the Hehner value practically represents the insoluble fatty acids alone. The proportion of unsaturated to saturated fatty acids is nearly 10 to 1. It is to the former that soy-bean oil owes its drying properties. It was observed that some of the oils examined remained perfectly clear, while others showed a considerable amount of foots and were therefore inferior in quality. It was also observed that, in general, light colored beans gave a paler oil than the dark colored varieties, also the oil appeared to dry more quickly. It is realized, however, that no conclusions may be drawn from this mere observation.

According to Toch,[4] cold-pressed soy-bean oil, heated to 500° C. for from 5 to 7 hrs., thickens like linseed oil and attains a specific gravity of 0.960 or more. Such an oil is certainly suitable for use in certain paints. In general, the latter are not as glossy and require somewhat longer to dry than linseed paints, but mixtures up to 33 per cent or even higher have given very good results in practical exposure tests. It is probably at its best when used in interior paints, baking japans, and in varnish. Soy-bean oil varnish requires longer to dry but is substantially like linseed varnish after a short exposure.

Analyses of two composite samples of soy-bean oil, obtained from sixteen different samples of Black Eyebrow soy beans were made, with the following average results: saturated fatty acids, 9.2 per cent; unsaturated fatty acids, 8.49 per cent. The values obtained by Thompson and Morgan[5] on a composite sample agree very well with these.

---

[1] Received February 17, 1920.

[2] Work done at Rutgers College and the New Jersey Agricultural Experiment Station, New Brunswick, N. J.

[3] *J. Soc. Chem. Ind.*, **31** (1912), 572; *Oil and Color Trades J.*, May **1913**.

[4] North Dakota Agricultural Experiment Station, *Special Food Bulletin* **21** (1913).

[5] Quoted from "Soya," a bulletin published by A.M. Parks, Importers, The Bourse, Philadelphia, Pa.

[6] Delaware Agricultural Experiment Station, *Bulletin* **98** (1912).

[1] Educational Bureau, Paint Manufacturers' Association of the United States, *Circular* **37**.

[2] *Ibid.*, **30**; *Bulletin* **53**.

[3] *Loc. cit.*

[4] *J. Soc. Chem. Ind.*, **31**(1912). 572; *Oil and Color Trades J.*, May **1913**.

[5] Delaware Agricultural Experiment Station, *Bulletin* **98** (1912)

Oil and Protein Content of Various Soy-Bean Varieties

Since the amount of oil contained in several varieties tested was exceedingly inconstant, this point was studied further. The amount of oil present in the seed, as well as its drying power, are important from the standpoint of the paint or varnish industry. The greater number of samples were secured from the variety plot tests which have been conducted at the N. J. Agricultural Experiment Station for several years. A few were obtained from seed houses in Newark and Philadelphia. The samples were partly dried to facilitate grinding, ground to pass a 40-mesh sieve, and stored in glass sample jars until analyzed. It was found that the oil was incompletely extracted in samples ground coarser than 40-mesh size. The Soxhlet method of extraction was used. Electric bulbs enclosed in an asbestos box furnished the necessary heat. The oil was extracted in 8 hrs., and good checks were obtained. The extraction flasks containing the oil were dried from 30 to 50 min. in a constant temperature electric oven at 100° C. to constant weight. Too long exposure caused the absorption of oxygen and a resulting increase in weight. This had to be guarded against throughout the whole experiment.

Nitrogen was determined by the Gunning modification of the Kjeldahl method. With 5 g. K_2SO_4, 1 g. $CuSO_4$, and 25 cc. H_2SO_4, a complete digestion could be carried out in 30 min. Table III gives the result of these analyses.

Table III

No. of Samples	Variety Soy Bean	Color	Average Per cent Oil	Average Per cent Protein (N × 6.25)	Color of Oil	Drying Power of Oil
8	Guelph	Green	21.2	38.1	Dark yellow	Poor
6	Ito San	Yellow	19.0	41.4	Straw	Fair
6	Cloud	Black	17.0	42.0	Dark straw	Poor
6	Hollybrook	Yellow	17.2	40.8	Straw	Good
6	Haberlandt	Yellow	19.2	38.3	Light straw	Good
8	Ebony	Black	14.6	43.6	Straw	Fair
4	Manhattan	Yellow	18.5	37.9	Straw	Good
6	Wilson	Black	18.8	37.3	Amber	Fair
6	Edna	Black	19.0	39.8	Straw	Fair
6	Tarheel	Black	16.1	39.0	Dark brown	Poor
6	Medium yellow	Yellow	19.6	39.3	Pale	Very good
6	Manchu	Yellow	21.6	40.5	Straw	Good
6	Ohio 9035	Yellow	21.5	37.3	Straw	Good
6	Swan	Yellow	19.1	42.5	Amber	Fair
6	Baird	Brown	17.9	43.0	Straw	Fair
172	Black Eyebrow	Black and yellow	20.2	38.7	Pale straw	Good
4	Ohio 7406	Yellow	17.0	40.1	Straw	Fair
16	Early Brown	Brown	19.5	40.3	Pale straw	Good
1	Habero	Yellow	17.2	41.4	Straw	Good
3	Amherst	Yellow	17.5	43.6	Straw	Good
3	Auburn	Black	21.6	40.0	Straw	Good
3	Manchuria	Yellow	23.2	36.9	Pale	Very good
1	O'Kute	Olive	25.6	35.7	Pale	Fair
6	Arlington	Black	16.7	43.4	Straw	Good
6	Peking	Black	17.9	37.3	Straw	Fair
1	Ogema	Brown	19.1	37.9	Straw	Good

The per cent of oil in soy beans is not at all constant, and the same thing is true of the nitrogen content. The range for oil in the twenty-six varieties tested is from 14.6 per cent in Ebony to 25.6 per cent in O'Kute.

The protein varies from 35.7 to 44.3 per cent. These data are valuable in that they show which varieties yield the largest quantity of oil as well as protein. Only high oil-yielding varieties should be planted by the farmer who is growing soy beans for their oil. Of course the question of yield per acre enters into any deliberations regarding the best oil producing varieties, and it is possible that some standard variety like Ito San or Ohio 9035 might actually give more oil *per acre* than O'Kute, with over 25 per cent oil. Still another factor must be considered, because the writer, as well as others, has noted[1] that, on account of the anatomical structure of the seed itself, the oil is more easily pressed from some varieties than from others. In those varieties where the oil content is high, it follows usually that the protein is low. For this reason the variety of soy bean that is best suited for oil production may not be best for feed.

There seems to be a correlation between the color of seed and drying power of the oil, but too much weight cannot be given this conjecture. In general, however, the dark-seeded varieties yielded oil of rather poor drying power. For example, Tarheel, Cloud, Black Eyebrow, and Guelph, all highly colored seeds, gave an oil which did not dry well. In the case of the Guelph variety, it seems certain that a portion of the coloring matter in the oil expressed from the seeds comes from the green seed coat.

The writer has shown elsewhere[1] that the inoculation of soy-bean plants with *B. radicocola, var. soy bean*, the nitrogen-fixing bacteria, causes a marked decrease in oil content of soy-bean seeds. A similar depression in oil content is noted where lime, in the form of the oxide or carbonate, is used as a soil amendment. Phosphates also increased the protein content of soy-bean seeds at the expense of oil. These differences are sometimes as great as 3 per cent in oil content—a factor of considerable importance.

Effect of Date of Planting upon Composition and Maturity of Soy Beans

Mooers,[2] as well as Garner, Allard and Foubert,[3] have shown that maturity in soy beans occurs much more rapidly when seed is planted late in the season. Working at Arlington, Va., the latter investigators found differences as great as 2 per cent in oil content between early and late planted seeds. This work was checked under New Jersey conditions as a result of the following experiments conducted with two varieties of seeds. The interval between plantings was about 2 wks. The criterion used for maturity was when most of the seed pods had turned brown. The data are presented in Table IV.

Table IV

No. of Plots	Variety	Date Planted	Date Matured	Days Required to Maturity	Oil in Seeds Per cent
2	Black Eyebrow	June 3	Sept. 10	99	18.92
2	Black Eyebrow	June 17	Sept. 15	90	18.70
2	Black Eyebrow	July 1	Sept. 23	84	18.30
2	Black Eyebrow	July 15	Oct. 4[1]	81	17.20
2	Black Eyebrow	August 1	Oct. 12[1]	72	17.00
2	Early Brown	June 3	Sept 13	102	19.60
2	Early Brown	June 17	Sept. 17	92	19.50
2	Early Brown	July 1	Sept. 28	89	19.30
2	Early Brown	July 15	Oct. 8	85	18.72
2	Early Brown	Aug. 1	Oct. 21[1]	81	18.68

[1] Frost hastened maturity and made observations more difficult.

These data show that the length of the growing season, or the number of days to maturity, is to a large degree dependent upon the time of planting. The yield of seed and forage was much less upon the late planted plots than upon those planted before July 1. The oil content of the seeds obtained by sampling the two plots of each series was higher in the case of the early plantings and fell off considerably as the date of planting became later and later. In the case of the Black Eyebrow variety, there was a difference of 2.9 per cent between the earliest and latest plantings. In the case of the Early Brown variety this difference amounted to but 0.92 per cent; yet in either case the difference is appreciable and constant. It seems therefore that for best results in growing soy beans for their oil, early, rather than late, plantings should be made.

Summary

1—Soy-bean oil is a semi-drying oil consisting largely of the glycerides of palmitic, oleic, linolic, and linoleic acids. Chemically it resembles corn oil but dries much better.

2—It may be used successfully to replace linseed oil in part in the manufacture of paints and varnishes. When used with suitable driers, such as lead, cobalt or manganese tungate or linoleate, it may be used alone, otherwise it is expedient to use mixtures of soy-bean oil up to 50 per cent with tung or linseed oils.

---

[1] Nemzek, *Loc. cit.*

[1] *Soil Sci.*, **6** (1918), 81.

[2] Tennessee Agricultural Experiment Station, *Bulletin* **82** (1908).

[3] *J. Agric. Res.*, **3** (1914) 227.

3—Domestic soy-bean oil is practically identical chemically and physically with the imported oils. Excellent soybean oil has been produced in this country, the whole Southern section of which is admirably suited to the growth of the beans.

4—Samples of soy-bean oil from different varieties of beans, subjected to different methods of extraction, length of storage, soil conditions, and maturity of the seed when harvested, vary considerably in their physical and chemical properties.

5—The average amount of oil obtained from twenty-six different varieties of soy-beans was 18.3 per cent; Ebony was lowest with only 14.8 per cent, while O'Kute was highest with 25.6 per cent. Such vast differences between varieties is of very great importance in growing soy beans for the oil market.

6—The length of growing season influences the oil content of soy-bean seeds. The oil content becomes less as the date of planting is later in the season. The number of days required to reach maturity is materially shortened when plantings are made during the middle and late summer. For growing soy beans as a catch crop or second crop on the same land, this fact is of prime importance.

7—There is considerable variation in the color and drying power of soy-bean oils derived from different varieties of soy beans.

The Alkalinity of Searles Lake Brine[1,2]

By Roger C. Wells

Division of Chemical and Physical Research, U. S. Geological Survey, Washington, D. C.

The article by J. E. Teeple[3] on the operations of the American Trona Corporation at Searles Lake approaches the ideal, in the opinion of the writer, in divulging to the public the methods and accomplishments of a large company that has carried on considerable chemical research, while at the same time specifying the particular points that have been made the subject of patent applications. The writer visited the plant of this company at Searles Lake in the fall of 1920 and was given an opportunity to inspect the equipment and methods of operation that Mr. Teeple describes. It is a great pleasure to express appreciation of the courtesies shown at that time.

The Searles Lake brine is a very interesting subject for investigation from a geochemical point of view as well as for its commercial value. Although it is recent, geologically speaking, it is changing so slowly, if at all, at the present time that the changes probably cannot be detected. It is possible, however, to determine the salts that separate on evaporation at various temperatures and the relation of certain physical properties of the brine to its components. The actual alkalinity of the brine, as measured by the H-ion concentration, is a property to which the writer has given some attention, with special reference to its use in arriving at a logical form of expression of the analysis of the brine. Very little has been published on the problem of determining carbonate and bicarbonate in the presence of borax and metaborate.

Analysis of Brine

The sample of brine on which the experiments described below were made was collected from Well 86, at a depth of 35 to 40 ft., Sept. 20, 1913, by W. B. Hicks, of the United States Geological Survey. It had stood in a quart glass bottle without being opened until the present determinations were made. The H-ion concentration was then found to be 3.32×1^{-10} at 25° C., or, as usually expressed pH = 9.48. The apparatus used in making this determination has been previously described.[1] The tabulated determinations were also made using the usual methods, such as are described in *Bulletin* 700 of the United States Geological Survey.

Determinations, Searles Lake Brine

	Per cent of Brine
K	2.46
Cl	12.32
SO_4	4.72
CO_2	1.84
B_2O_3	1.04
Specific gravity at 25°	1.294

1 cc. requires 13.1 cc. 0.1 *N* HCl with methyl orange

1 cc requires 12.85 cc 0.1 *N* HCl with *p* nitrophenol

1 cc. requires 3.80 cc 0.1 *N* NaOH to phenolphthalein end-point after removing CO_2 and making exactly neutral to *p* nitrophenol

Conversion of Analytical Results

The next problem is to convert the above determinations into the form of salts, which is the most logical form of expression for several reasons: First, the brine as it comes from the lake has been in contact with various salts, and similar salts can be obtained from it by evaporation. Second, after calculating the potassium to some one salt, such as potassium chloride, all the other salts may be expressed as sodium salts. Third, the actual pH alkalinity of the brine lies between the limits shown by solutions of sodium carbonate and sodium bicarbonate on the one hand and sodium tetraborate (borax) and sodium metaborate on the other. The special problem here is to convert the total CO_2 found into Na_2CO_3 and $NaHCO_3$ and the total B_2O_3 into $Na_2B_2O_4$ and $Na_2B_4O_7$. Titration methods are of no avail because there are four salts to be titrated and the titration curve gives no sharp breaks for the various salts. Modes of expression based on arbitrary assumptions lead to confusion unless the assumptions have some logical basis, and for this reason attempts to convert the CO_2 and B_2O_3 into only two or three salts are unsatisfactory, because the chemist realizes that any such that could be chosen would react on each other if dissolved, producing at least the four salts that have been mentioned. The writer has sought to overcome these difficulties by determining in separate experiments what proportions of the salts of each buffer pair, *i. e.*, the carbonates and the borates, would be required to give the same pH value as found for the brine. He has also shown that if the proportions found for one pair are taken to represent the concentrations of those two salts in the brine, the proportions for the other pair must be as determined. The results obtained appear to yield a form of expression that is free from the above objections.

ARTIFICIAL BRINE—An artificial brine containing only sodium chloride, potassium chloride, and sodium sulfate in the concentrations found in the Searles Lake brine was made up to serve as a medium to which buffer salts could be added in various amounts, thus making any possible "salt effect" constant and equal to that in the Searles brine. A set of pH determinations was made with this brine after adding various proportions of sodium carbonate and bicarbonate, keeping the total CO_2 equal to that found in the Searles brine. A similar set was made with mixtures of borax and sodium metaborate, keeping the total B_2O_3 the

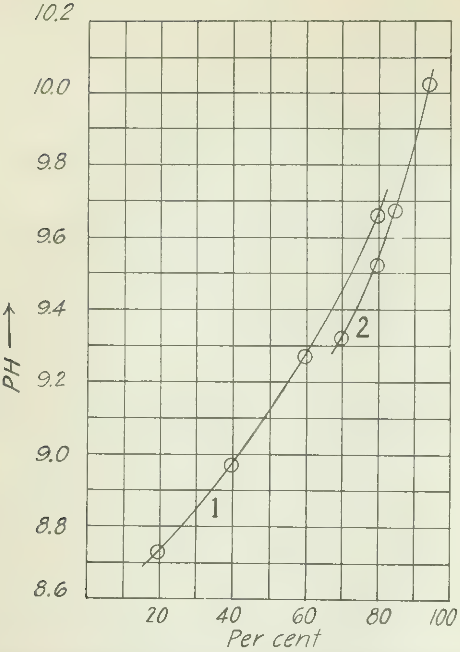
---

[1] Received April 1, 1921.

[2] Published by permission of the Director of the U. S. Geological Survey.

[3] This Journal, **13** (1921), 249.

[1] *J. Am. Chem. Soc.*, **42** (1920), 2160.



pH FOR MIXTURES OF $Na_2B_4O_7$ AND $Na_2B_2O_4$, AND OF $NaHCO_3$ AND Na_2CO_3 IN SEARLES LAKE BRINE. CURVE 1—PER CENT OF TOTAL B_2O_3 PRESENT AS $Na_2B_2O_4$. CURVE 2—PER CENT OF TOTAL CO_2 PRESENT AS Na_2CO_3

same as found in the Searles brine. The metaborate was produced by the addition of the necessary quantity of a strong caustic soda solution to borax. In the experiments with the borate buffers they were added to a slightly more concentrated solution in order that the water of composition should yield the same final dilution as in the Searles brine. The results of H-ion determinations on these mixtures are given in Table I, and plotted in the accompanying figure.

TABLE I—RESULTS OF pH DETERMINATIONS MADE BY ADDING (*a*) CARBONATE AND (*b*) BORATE BUFFERS TO AN ARTIFICIAL BRINE RESEMBLING SEARLES LAKE BRINE

Percentage of Total CO_2 Present as Na_2CO_3	pH	Percentage of Total B_2O_3 Present as $Na_2B_2O_4$	pH
94	10.02	80	9.66
85	9.67	60	9.27
80	9.52	40	8.97
70	9.32	20	8.73

When the pH values are plotted against the percentages in each case, the results are found to give smooth curves, from which it is easily seen that in order to yield the value pH = 9.48 the total CO_2 and B_2O_3 should be distributed as follows in the respective salts:

$$CO_2 \begin{cases} \text{78 per cent as } Na_2CO_3 \\ \text{22 per cent as } NaHCO_3 \end{cases} \qquad B_2O_3 \begin{cases} \text{71 per cent as } Na_2B_2O_4 \\ \text{29 per cent as } Na_2B_4O_7 \end{cases}$$

or, as percentages of the brine:

$$Na_2CO_3 = 3.46 \qquad Na_2B_2O_4 = 1.39$$
$$NaHCO_3 = 0.77 \qquad Na_2B_4O_7 = 0.43$$

It seemed reasonable to suppose from the principles of equilibrium in salt solutions that two mixtures of buffer salts yielding the same pH value in separate equal portions of a given medium would show no change in pH when dissolved together in a single portion, but in order to strengthen this assurance all four salts were dissolved in the artificial brine in the proportions last mentioned and the solution tested. The pH value found was 9.50, which agrees well with the value 9.48, on which the proportions of the buffers were based, and proves that there is no reaction of the buffer salts on each other when they are taken in the proportions that give the same pH values separately.

In Table II is given the analysis of Searles Lake brine in the form deduced from the present study, together with Teeple's analysis and an earlier one based on determinations by W. B. Hicks,[1] for comparison.

TABLE II—ANALYSIS OF SEARLES LAKE BRINE

	Wells	Teeple	Hicks
KCl	4.69	4.82	4.00
NaCl	16.63	16.54	17.27
Na_2SO_4	6.98	7.16	6.48
Na_2CO_3	3.46	4.17	4.65
$NaHCO_3$	0.77	0.52	.....
$Na_2B_2O_4$	1.39	0.85	...
$Na_2B_4O_7$	0.43	0.85	1.42
H_2O	65.65	65.09	66.18
TOTAL	100.00	100.00	100.00

Another interesting characteristic of the brine from the geochemical point of view is its carbon dioxide tension. Will the brine gain or give off carbon dioxide on exposure to the atmosphere? To answer this question 100 cc. of the brine were agitated in a thermostat at 23° C. by means of a vigorous current of filtered and washed outdoor air for 111 hrs. During the first 15 hrs. the total carbon dioxide content remained practically unchanged when referred to the same volume; but meanwhile the brine was very slightly diluted, so that the proportion of carbon dioxide in the total salts increased slightly. On further treatment the proportion of carbon dioxide in the total salts appeared to remain nearly constant, as shown in Table III.

TABLE III—TOTAL CO_2 IN SEARLES BRINE BEFORE AND AFTER AGITATION WITH OUTDOOR AIR

Time of Agitation Hours	CO_2 per Liter Grams	Specific Gravity of Brine	Estimated Total Salts per Liter	Percentage of CO_2 in Total Salts
0	23.78	1.294	451.9	5.26
15	23.80	1.289	443.0	5.37
63	23.06	1.283	433.1	5.32
111	22.59	1.274	418.1	5.40

As the slight increase in CO_2 in the total salts may be due to the increased dilution and accompanying hydrolysis, it seems fairly safe to conclude from the above results that the brine is very nearly in equilibrium with the atmosphere so far as its content of carbon dioxide is concerned.

Fertilizer Imports

During the ten-month periods ending in April 1921 and April 1920, imports of fertilizers (in long tons) in the United States were as follows:

	1920	1921
Ammonium sulfate	2,117	2,011
Bone dust, ash meal	5,354	26,237
Calcium cyanamide	72,510	33,516
Guano	14,045	37,519
Kainite	202,430	202,076
Manure salts	217,064	123,168
Potassium salts:		
Muriate	99,843	48,442
Sulfate	5,344	11,368
All other fertilizers	93,378	108,327
TOTALS	712,085	592,664
Sodium nitrate (not included in above table)	605,436	768,121

The War Department is to distribute more than 12,000,000 lbs. of picric acid to farmers for agricultural purposes. This surplus stock accumulated for war purposes, is located at Sparta, Wis., and Wingate, N. M., and will be distributed through the Bureau of Public Roads of the Department of Agriculture, the only cost to farmers being freight charges and six cents a pound for placing the powder in the necessary cartridges.

---

[1] United States Geological Survey, "Mineral Resources," 1917, II, 411.

Action of Lime on Greensand[1,2]

By R. Norris Shreve

43 Fifth Avenue, New York, N. Y.

In the last few years a great deal of work has been done on the extraction of potash from various minerals, such as feldspar, leucite, mine tailings, greensand, etc. For the purpose of liberating the potash, treatment with lime or with a mixture containing lime has been employed rather extensively. This paper gives the results of close study of the action of lime in the presence of water upon greensand or glauconite.

To show the importance of greensand, it may be mentioned that this raw material underlies the surface of hundreds of square miles of the State of New Jersey in beds of commercial value, and within reach of a steam shovel.

The process discussed herein has been in actual operation at a small manufacturing plant for several years, and in its early stages was described by H. W. Charlton.[3] In outline, this process as now employed consists in heating a slurry made from 1 part of ground greensand, 1 part of lime, and 5 parts of water or weak washings in a digester for about 1 hr., at a temperature around 470° F., and under sufficient pressure to keep the water in the liquid phase. This will be somewhat over 500 lbs. pressure.

The chief reaction which takes place is that of the lime upon the greensand, which on the one hand liberates the potash in the form of a very pure caustic potash, and on the other hand produces a material high in lime which possesses valuable cementitious and liming properties.

An analysis of greensand that has been commercially used is given herewith:

Typical New Jersey Greensand

		Per cent
Silica	SiO_2	49.8
Alumina	Al_2O_3	9.8
Iron (figured as)	Fe_2O_3	18.0
Lime	CaO	0.9
Magnesia	MgO	7.7
Potash	K_2O	7.4
Soda	Na_2O	0.4
Sulfuric acid	SO_3	0.24
Phosphoric acid	P_2O_6	0.25
Loss on ignition	...	5.6
	Total	100.1

The action of the lime has been studied from the following aspects:

1—Effect of state of division of the greensand (Table I).
2—Effect of temperature of digestions (Table II).
3—Effect of ratio of water used (Table III).
4—Effect of substituting KOH solutions for the water (Table IV).
5—Effect of variations in lime used (Table V).
6—Effect of addition of various salts (Table VI).

Apparatus

The method of conducting the experimental work offered various difficulties, and a number of different types of apparatus or digesters were tried. Finally the writer had built a multiple digester somewhat similar to that described by H. D. Gibbs and Max Phillips,[4] which gave very satisfactory results with a minimum of time and effort. This multiple digester consisted of a molten metal bath (tin and lead in equal parts) heated by gas burners, and a carriage, so arranged as to revolve in the molten metal. This carriage held six cylinders which were rotated while immersed in this hot metal. The whole moving parts were so arranged that a quick removal could be made in order to take out one or more cylinders for cooling in water and analysis. The individual cylinders measured about 3 in. in diameter by 12 in. long and were similar to those used for shipping nitrous oxide. Each cylinder took a typical charge of:

	Grams
Greensand	85
Quicklime	85
Water	425

The control of temperature was within 5° to 10° F., at around 475° F., which was considered very good; furthermore the initial heating of the cylinders when plunged into the hot metal was rapid, taking only a few minutes.

Experimental Details

In general the experimental work indicated that the most economical yields of potash were obtained by heating under agitation a slurry of

	Parts
Finely ground greensand	1.0
Quick lime	0.9
Water or weak washings	5.0

at a temperature of 470° F., under a pressure of about 550 lbs., for 40 min. In this case about 61 per cent of the potash in the greensand was converted into the soluble form. In the presence of various accelerators, such as nitrates, the conversion was increased to 81 per cent. The details of the experimental work are given in the following tables:

Table I—Effect of State of Division of Greensand

Expt. No.	Condition of Greensand	Per cent Potash Converted 40 Min. at 470°–480° F.
B 58	Unground	16.8
B 61	Ground, 90% 200 mesh, calcined	75.6
B 66	Duplicate	72.3
B 67	Unground, calcined	17.5
B 19 B 21 B 22 B 26	Ground, 90% 200 mesh	60 (Av.)

Table I shows the importance of fine grinding, and this is to be expected, as the action of the lime can only be on the surface of the solid particles. Agitation during digestion increases the yields, and violent agitation is very effective; it is, however, not practical to carry this out on a large scale, and we have secured the same result by allowing the digestion to proceed for a somewhat longer interval.

Table II—Effect of Temperature of Digestion

Expt. No.	Temperature ° F.	Time of Digestion	Per cent Potash Converted
		Medium Temperature	
B 29	400–414	10	26.1
B 28	398–412	40	43.5
B 36	389–397	60	44.2
B 33	398–402	60	56.4
B 32	389–401	120	56.2
B 35	389–398	120	58.8
		High Temperature	
M 19	470–480	20	47.5
M 20	470–480	40	65.3
M 21	470–480	60	68.8
M 22	470–480	90	74.2
M 23	470–480	120	77.9
M 24	470–480	240	83.4

A great many experiments indicated that the yield at 470° to 480° F. was very much higher than at temperatures up to 425° F. The results shown in Table II indicate that the recovery of potash from a digestion of 40 min. at 470° to 480° F. (about 500 lbs. steam pressure) is higher than from a digestion of three times that interval at 390° to 400° F. (about

---

[1] Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] The work described in this paper has been done in the laboratories of the Eastern Potash Corp., for the improvement of the process to be used at the large plant now under construction at New Brunswick, N. J. This plant will treat 1000 tons of the greensand per day, with about 900 tons of quicklime, and will produce about 65 tons of caustic potash per day, or an equivalent amount of other potash salts, *e. g.*, nitrate. In addition to the potash salts, the plant will turn out several thousand tons per day of a high lime carrying material.

[3] This Journal, **10** (1918), 6.

[4] "Alkali Fusions," *Ibid.*, **12** (1920), 145.

225 lbs. steam pressure). The digesters for the large-scale plant are accordingly being built to work at 500 lbs. pressure.

TABLE III—EFFECT OF RATIO OF WATER USED

EXPT. No.	Ratio Greensand: Lime: Water	Time of Digestion Minutes	Per cent Potash Converted
B 4	1:1:5	10	57.0
B 9	1:1:6	10	54.4
B 10	1:1:7.5	10	56.5
B 11*a*	1:1:10	10	60.0
B 11*b*	1:1:10	10	55.1
B 21	1:1:5	40	59.1
B 20	1:1:6	40	63.9
M 19	1:1:5	20	47.5
M 25	1:1:10	20	58.2
M 20	1:1:5	40	65.3
M 26	1:1:10	40	68.9
M 21	1:1:5	60	68.8
M 27	1:1:10	60	75.1
M 22	1:1:5	90	74.2
M 28	1:1:10	90	76.1
M 23	1:1:5	120	77.9
M 29	1:1:10	120	78.1
M 24	1:1:5	240	83.4
M 30	1:1:10	240	85.6

The most concentrated slurry that can be handled economically is the one with a 1 : 1 : 5 ratio of greensand, quicklime, and water. It was of interest to determine whether increase in dilution would sufficiently increase the potash recovery to pay for the handling of the larger amounts of solutions, which, in case of the 1:1:10 ratios shown in Table III, would mean the increase of the primary potash liquor from 5000 to 10,000 tons per 24 hrs. The table shows a slightly greater yield with the doubling of the amount of water, which yield is, however, not increased as much for the longer intervals of digestion as for the first 10 or 20 min. It is more economical to secure the greater recovery by digesting for a longer period than to handle and evaporate the larger bulk of solution.

TABLE IV—EFFECT OF SUBSTITUTING CAUSTIC POTASH SOLUTIONS FOR WATER IN THE 1:1:5 RATIO OF GREENSAND, LIME, AND LIQUID

EXPT. No.	Per cent Strength Caustic Potash Solution Used	Per cent Potash Converted 40 Min at about 470°–480 ° F.
B 19 B 21 B 22 B 26	Water	60 (Av.)
B 60	0.5	57.8
B 59	1	58.5
B 48	1	28.3 (?)
B 57	1	47.6
B 49	2	61.9
B 50	3	73.5
B 51	5	61.4
B 52	10	59.6
B 30	20	62.3
M 12	Water	61.7
M 7	0.5	54.8
M 8	1	50.0
M 9	2	49.4
M 10	3	49.6
M 11	10	54.2

The possibility occurred to the writer of dividing the plant in halves, running one-half in series with the other, and thus making the potash liquor of the first half the "make up" liquor for the second half. To determine whether this could be done, the effect was studied of substituting potash liquors of various strength for the water in the slurry. Table IV gives the results and indicates that while there is a noticeable decrease in the potash recovery, yet such caustic potash solutions can be practically substituted for water. The limit to this working of parts of the plant in series is set by the amount of weak washings obtained from the filtration units, which of course must be taken care of in the "make up."

TABLE V—VARIATIONS IN LIME RATIO AT DIFFERENT DIGESTION PERIODS

(All at high temperature of about 470°–480° F.)

EXPT. No.	Ratio Greensand: Quicklime: Water	Quicklime Used Grams	Equivalent CaO Used Grams	Free CaO in Residue Grams	CaO Consumed Grams	Time Digestion Min.	K_2O Converted Per cent
B 40	1:0.5:5	42.5	39.5	0.0	39.5	40	46.5
B 39	1:0.6:5	51.0	47.5	0.7	46.8	40	50.8
B 38	1:0.75:5	64.0	59.5	11.1	48.4	40	57.5
B 37	1:0.9:5	76.5	71.2	21.1	50.1	40	61.0
B 43	1:1:5	85.0	79.1	23.2	55.9	40	62.9
B 47	1:1:5	85.0	79.1	29.3	49.8	40	63.6
B 42	1:1.25:5	106.3	98.8	41.8	57.0	40	62.2
B 41	1:1.5:5	127.5	118.6	57.1	61.5	40	57.3
B 45	1:1.5:5	127.5	118.6	64.4	54.2	40	68.8
B 53	1:1:5	85.0	79.1	17.2	61.9	80	69.6
B 55	1:1.5:5	127.5	118.6	49.3	69.3	80	65.6
B 54	1:1:5	85.0	79.1	14.4	64.7	120	73.8
M 6	1:0.6:5	51.0	47.4	0.0	47.4	40	53.1
M 5	1:0.75:5	63.75	59.3	11.5	47.8	40	54.6
M 4	1:0.8:5	72.25	67.2	16.6	50.6	40	58.6
M 3	1:0.9:5	76.5	71.1	21.7	49.4	40	58.3
M 2	1:1:5	85.0	79.1	29.4	49.7	40	59.8
M 1	1:1.25:5	106.25	98.8	43.3	55.5	40	61.3

It was difficult to carry out accurate analyses of the experiments listed in Table IV. The liquor could not be analyzed with the accuracy necessary to determine the increment of potash, hence the residue was washed free of soluble potash and the unconverted K_2O determined.

As a saving of 10 per cent of the lime used amounts to 100 tons per day, a careful investigation of the recovery from different ratios of lime was carried out, and the results shown in Table V. In these experiments, after the filtration of the potash liquor, the solid residue was washed with alcohol so as not to dissolve out any of the $Ca(OH)_2$, and the residue was analyzed for total CaO and for free $Ca(OH)_2$. For the determination of the free $Ca(OH)_2$ in the presence of calcium silicates, etc., the very excellent method of W. E. Emley was employed.[1]

In the table the results are figured to CaO from the analyses of both the quicklime used and the residue obtained, and the difference indicates the "CaO consumed." In Table V, this value is given in grams, and it is the weight of CaO that reacted with 85 g. of greensand. We concluded from these and other similar results that the ratio of lime to greensand could be cut to 0.9 part and possibly a little lower.

It is a matter of great interest to know just what occurs in such reactions as these. The microscope indicates the presence of calcium monosilicate in the solid residue obtained from the reaction. If all the silica in the 85 g. of greensand used, namely, 42 g., would react to form the monosilicate, there would be required 39 g. of CaO, or double this amount for the dicalcium silicate. The table shows a "consumption" of free CaO of about 50 g. (except where a very large excess of lime was used over a period longer than 1 hr.). Realizing that all the silica may not react, but also that the alumina probably reacts and consumes some lime, it seems likely that the main product of the reaction is calcium monosilicate.

TABLE VI—EFFECT OF ADDITION OF VARIOUS SALTS

(In each experiment a ratio of 1 : 1 : 5 was used for the greensand, lime, and water. The temperature of digestion was about 470° to 480° F.)

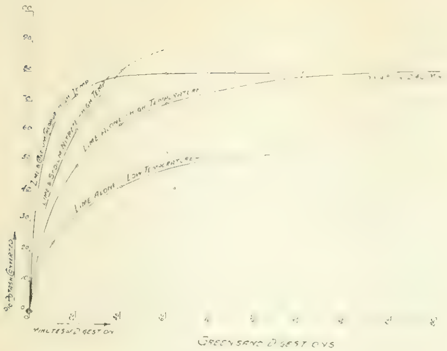
EXPT NO.	SALT ADDED		Time of Digestion Min.	Per cent Potash Recovered
Several	Blank, water only for comparison		40	61 (Av.)
M 37	Calcium chloride, 10.0 g.		10	64.6
M 31			20	74.3
M 32			40	77.5
M 34			60	78.7
M 35			90	79.3
M 36			120	80.4
M 49	Sodium nitrate, 10.1 g.		10	39.7
M 50			20	61.1
M 51			30	67.5
M 52			40	80.9
M 53			60	83.9
M 56	Potassium nitrate	3.0 g.	40	62.8
M 55		6.0 g.	40	66.9
M 58		12.0 g.	40	64.1(?)
B 68		12.0 g.	40	69.0
B 70		12.0 g.	40	69.0
M 57		24.0 g.	40	68.5
M 59	Potassium nitrate (with only 0.9 part of lime)	12.0 g.	40	68.5
M 60	Potassium nitrate (with only 0.75 part of lime)	12.0 g.	40	64.4
B 69	Calcium nitrate	9.8 g.	40	73.7
M 41	Sodium sulfate 99 per cent	6.7 g.	40	70.3

CONVERSION OF POTASH INTO SALTS

As there is not a market in the United States for the annual production of caustic potash from the proposed plant, we naturally planned for other potassium compounds. The writer approached this problem with the idea of so trans-

---

[1] *Trans. Am. Ceram. Soc.*, **17** (1915), 720.



forming the caustic potash as to preserve the hydroxyl part of the caustic as well as the potassium. Experiments indicated that the following reactions worked:

$$KOH + NaNO_3 = KNO_3 + NaOH$$
$$2KOH + Na_2SO_4 = K_2SO_4 + 2NaOH$$

A number of other similar reactions were also successfully tried, but these were the two of most interest. After we had worked on the potassium nitrate for some time, we found that during the time of the Crimean War much potassium nitrate was made in a similar fashion, the caustic potash being derived from the liming of wood ashes.

It then occurred to the writer to add the $NaNO_3$ in the primary digestion charge, and thereby to produce KNO_3 and NaOH directly. This worked very successfully, but the surprising observation was made that the recovery of potash was increased from 61 per cent to 81 per cent. In other words, the presence of the $NaNO_3$ accelerated the action of the lime on the greensand. This led to an investigation of the action of other salts. The most important of such accelerators are summarized in Table VI. Among other accelerating salts are: sodium chloride, sodium chlorate, sodium phosphate, sodium nitrite, sodium sulfite, sodium acetate, sodium bromide, sodium silicofluoride, sodium fluoride, sodium hypochlorite, etc. Ammonium chloride also acted similarly. Potassium chloride had no effect.

The action of calcium chloride is to produce potassium chloride. This has been previously studied and patented for the Company by H. W. Charlton, who has helped on the other work and has arranged patent protection on the action of the nitrate, etc.

In the use of potassium nitrate in the original charge there is no reaction, but simply an acceleration of the attack of the lime, as the potassium nitrate is recovered and used again. In this case caustic potash is produced.

The apparent explanation of the accelerating action of these salts lies in the fact that they increase the solubility of the $Ca(OH)_2$ in the water and in the weak caustic solutions.[1]

The curves shown in the figure summarize the most important facts brought out in the tables in a comparative manner and they are self-explanatory.

SUMMARY

Tables are given showing the action of lime on greensand under various conditions. To secure economic recovery of the potash the following conditions are indicated:

1—Fine grinding; that is, 90 per cent through 200 mesh.

2—Digestion at around 470° to 480° F. for 1 hr.

3—A charge ratio of greensand, quicklime, water and weak caustic solution of 1 : 0.9 : 5.

4—Addition of various salts for the purpose of:
  (a) Accelerating the reaction.
  (b) Changing the potassium hydroxide to other potassium compounds.
  (c) Both accelerating and changing to other compounds.

In particular, if caustic potash is desired, potassium nitrate is added as an accelerator; while, if potassium nitrate is wanted as the primary product, sodium nitrate is added to the charge; caustic soda is also produced as a valuable by-product in the latter case.

ACKNOWLEDGMENT

Acknowledgment is made to Messrs. M. Hauber, Jr., and Oscar Newman who carried on the laboratory work reported here.

---

[1] Gmelin-Kraut, "Handbuch der anorganischen Chemie," II, 2, 207.

Platinum Production

Estimates of the production of crude placer platinum in the United States in 1920 give Alaska 27 oz., California 656 oz., Oregon 23 oz., and Washington 8 oz. Refiner reported a production of 41,544 troy oz. of new platinum metals in 1920, of which 36,015 oz. were platinum, 418 oz. iridium, 409 oz. osmiridium, 4309 oz. palladium, and 393 oz. of the minor metals, including rhodium and osmium. This represents a decrease of 3565 oz. compared with the 1919 production. 57,710 oz. of secondary platinum metals were also produced in 1920, representing a decrease of 3806 oz. as compared with 1919. Platinum metals imported for consumption in 1920 included 80,955 oz. of crude platinum and unmanufactured ingots, bars, sheets, etc., of which approximately 58,009 oz. are believed to be refined metal; 4718 oz. of iridium; 4473 oz. of osmiridium; 6944 oz. of palladium; 2675 oz. of the minor metals; and 781 oz. of manufactured platinum ware. This was 32,492 oz. more than in 1919. The consumption of platinum metals in the United States in 1920 was 141,041 oz., of which the jewelers took 57 per cent, the electrical industry 19 per cent, the dental industry 11 per cent, the chemical industry 10 per cent, and miscellaneous uses 3 per cent. The stocks of platinum metals at the end of 1920 amounted to 67,508 oz., which is an increase of 55 per cent as compared with the stocks at the end of 1919.

Reduction of Staff at Helium Plant No. 3

Orders have been issued to reduce the staff at Government Helium Plant No. 3 at Petrolia, Texas, and to place the heavy machinery in stand-by condition for the present. The plant has been operated intermittently on an experimental basis since its erection during the war, and it now seems advisable, in view of extreme lack of funds, to work with a smaller unit while accumulating the data necessary for conversion into an economical operating plant. Plant No. 3 has been drawing on the same supply of gas as the large production plant at Fort Worth operated by the Navy, which is now in operation, and since success is contingent upon a steady flow of gas of fairly uniform composition, Plant No. 3 is to be held in reserve while the Fort Worth plant is being brought up to full-scale steady operation. The Petrolia plant has produced helium of 60 per cent purity and has made repeated runs of considerable duration yielding gas of lower purity, but in view of the expense incurred in reprocessing the gas to bring it to the standard for balloon use the Bureau of Mines has endeavored to obtain first run gas of satisfactory purity. The ultimate purpose of the experiments is to provide a plant which shall furnish helium at a much lower cost than is possible by any known operative system.

The Determination of Small Quantities of Zinc[1]

By M. Bodansky

Laboratory of Biological Chemistry of the School of Medicine, University of Texas, Galveston, Texas

Quantities of zinc too small to weigh cannot be determined gravimetrically or electrolytically. In dealing with quantities ranging between 0.1 and 5 mg. the volumetric procedures are equally inadequate. A turbidimetric method based upon the precipitation of zinc by potassium ferrocyanide has been described recently by Breyer.[2] This method has been applied by Meldrum[3] in the quantitative determination of zinc in water, and by Birckner[4] in determining the zinc content of various food products. According to Birckner's procedure, the zinc is precipitated as the sulfide from a formic acid solution, filtered, and dissolved in hydrochloric acid. The turbidimetric comparison is performed on this solution in Nessler jars, if the amount of zinc is below 0.5 mg. With larger amounts aliquot portions are taken for comparison. Birckner states that the method gives reliable results, and if properly carried out the experimental error should not exceed ±0.05 mg. Owing to the sensitiveness of the turbidimetric comparison the method was used in this laboratory in an investigation of the zinc content of marine organisms,[5] and our experience as to its applicability confirms Birckner's findings.

Modifications of Breyer-Birckner Method

However, it was found necessary to modify the preliminary procedure. The material for analysis was prepared, ashed, and the copper removed as previously described by Rose and Bodansky.[6] The filtrate obtained from the copper sulfide precipitation was boiled to remove the hydrogen sulfide and made alkaline with ammonia. This solution was acidified with citric acid and the zinc was precipitated as the sulfide. The tendency of zinc sulfide to form colloidal suspensions when precipitated from acid and even from alkaline solutions and the difficulties involved in filtering such precipitates are well known. Where zinc occurs in traces this tendency is especially marked, and the introduction of a considerable error is almost unavoidable. By using citric acid in our analyses of marine organisms there was frequently obtained, during the heating preliminary to the introduction of the hydrogen sulfide, a precipitate of calcium citrate, the calcium being derived from the chitinous protective covering of some of the animals or from the skeletal structures of the marine vertebrates. It was noted that in the presence of calcium citrate the filtrates were clear and free of zinc. The calcium citrate is not an interfering substance and may be dissolved along with the zinc sulfide, and the zinc determined turbidimetrically as in Birckner's procedure.

The more complete recovery of minute quantities of zinc in this way may be due to the adsorption of the colloidal zinc sulfide particles by the calcium citrate. Indeed, Bancroft[7] has recently pointed out that there is some evidence to show that when a colloidal solution is precipitated the finer particles attach themselves to the coarser ones. As the turbidimetric method afforded a means for the estimation of minute quantities of zinc, a brief study of the behavior of colloidal zinc sulfide in the presence of calcium citrate was possible. Furthermore, in anticipation of future work on the occurrence and distribution of zinc in various tissues, it became necessary to study the precipitation of zinc sulfide in the presence of calcium citrate and to determine the applicability of such a method.

Precipitation of Zinc Sulfide in Presence of Calcium Citrate

zinc sulfide suspension—For preliminary experiments, a zinc sulfide suspension was prepared according to the method of Müller.[1] One gram of zinc was treated with sufficient sulfuric acid to dissolve it, and diluted with 30 cc. of glycerol and 100 cc. of distilled water. Five hundred cc. of ammonium sulfide solution were then added, and the whole diluted to 1 liter and allowed to stand for several days. One hundred cc. of Müller's suspension and 50 cc. of glycerol were gradually diluted to 1 liter with hydrogen sulfide water, shaking vigorously after each dilution. The suspension of finely divided zinc sulfide prepared in this way was not permanent, but when diluted with water, preparations were obtained which resembled very closely the zinc sulfide suspensions that are frequently formed during a precipitation.

To determine qualitatively the degree of subdivision of the zinc sulfide particles, 10-cc. portions of the suspension, equivalent to 1 mg. of zinc, were filtered cold through four grades of filter papers, 9 cm. in diameter; the residues were carefully washed with small portions of 2 per cent ammonium thiocyanate[2] and the amounts of zinc in the residues as well as in the filtrates were determined turbidimetrically. The results given in Table I show that only from 30 to 60 per cent of the zinc sulfide particles in the suspension are retained by filter papers of good make, such as are frequently used in qualitative and quantitative analysis. The limitations of the turbidimetric comparison do not permit of a closer approximation than that given in the table.

Table I—Retention of Zinc Sulfide Suspension by Standard Filter Papers

(10 cc. zinc sulfide suspension ≎ 1 mg. Zn filtered cold)

Filter Paper	Zinc Recovered Mg. Residue	 Filtrate	 Total
1	0.39	0.60	0.99
2	0.60	0.43	1.03
3	0.45	0.57	1.02
4	0.31	0.75	1.06

addition of calcium citrate—By using varying dilutions of the zinc sulfide suspension, with and without the addition of calcium citrate, and going through the usual analytical procedure, comparative data have been obtained on the adsorptive (?) effect of calcium citrate. Four series of determinations were performed on definite volumes of the suspension, varying in zinc content from 0.1 to 10.0 mg. In the experiments of Series I, measured portions of the suspension were diluted to 125 cc. After boiling these solutions for 15 min., a rapid stream of hydrogen sulfide was passed through the liquids until they had cooled to about room temperature. After allowing the precipitates to settle for 2 hrs., the flasks were heated on the water bath for 30 min. The precipitates were collected on small filters,[3] washed with 2 per cent ammonium thiocyanate, dissolved in hot hydrochloric acid, and the zinc was estimated turbidimetrically in the total volume or in an aliquot portion. In Series II, the suspensions were diluted to 115 cc. and treated with 10 cc. of 50 per cent citric acid. In Series III, 10 cc. of citric acid solution and 4 g. of calcium citrate, prepared from Merck's calcium carbonate and citric acid, were added in each experiment. In Series IV, the dilutions were made to 109 cc., and there were added 16 cc. of citric acid solution and 2.1 g. of calcium carbonate. In these experiments the calcium citrate precipitated as the solutions were boiled, the amounts separating approximating the undissolved portions of calcium citrate obtained in the experiments of Series III. The same procedure as detailed for Series I was closely adhered to in all the experiments. An examination of the results in Table II shows that the presence of calcium citrate facilitates the complete recovery of zinc as the sulfide, and that this is especially marked in the case of quantities less than 2.5 mg. Where zinc is present in higher concentrations complete recovery may be obtained in the absence of calcium citrate, as is indicated by the results obtained with 10-mg. quantities. This is probably due to the formation of a number of coarse zinc sulfide particles sufficient to adsorb the finer ones. It should also be noted that the recovery of the zinc sulfide is somewhat more complete when the calcium citrate is precipitated in the solution than when added pre-formed.

---

[1] Received March 14, 1921.

[2] W. W. Scott, "Standard Methods of Chemical Analysis," New York, 2nd Edition, 1917, 487.

[3] *Chem. News*, **116** (1917), 295, 308.

[4] *J. Biol Chem.*, **38** (1919), 191.

[5] Bodansky, *Ibid.*, **44** (1920), 399.

[6] *Ibid.*, **44** (1920), 99.

[7] This Journal, **13** (1921), 153.

[1] *Chem.-Ztg.*, **28** (1904), 35.

[2] Compare Jamieson, This Journal, **11** (1919), 323.

[3] Whatman No. 40.

Table II—Recovery of Finely Divided Zinc Sulfide in the Absence and in the Presence of Calcium Citrate

Zinc Present Mg.	Zinc Found Mg. Series I	Series II	Series III	Series IV
0.10	....	.....	0.08	0.11
0.20	0.06	0.06	0.15	0.18
0.30	0.12	0.09	0.26	0.28
0.40	0.16	0.21	0.36	0.39
0.50	0.16	0.20	0.47	0.48
1.00	0.75	0.68	1.00	0.99
2.50	2.20	2.28	2.20	2.40
10.00	8.96	10.32	10.20	10.40

Effect of Iron Salts

As is known, zinc sulfide, precipitated in the usual way, may retain traces of iron, and it was to be expected that the retention of this metal would be even greater in the presence of calcium citrate. The presence of iron in the solution to be used for the turbidimetric estimation should be avoided, because in the presence of ferrous salts there is produced potassium ferri-ferrocyanide which imparts a blue color to the solution. In our analyses of animal tissues known to contain appreciable quantities of iron, the interference due to this metal was not always experienced, and when it did occur one reprecipitation usually sufficed to make the final filtrate iron-free. To test the method further and to study the removal of iron salts, the experiments recorded in Table III were performed. In the experiments of Column A the zinc was precipitated as the sulfide from a citric acid solution. In those of Column B the precipitations were performed in the presence of 5 mg. of ferric chloride and sufficient calcium carbonate to give on boiling about 1 g. of calcium citrate. In Expts. 1B, 3B, and 5B, two precipitations, and in 2B and 4B, three precipitations were required to remove the iron. As will be observed, even under these conditions the zinc was almost entirely recovered.

Table III—Comparison between the Original Method and the Modified Procedure

Expt. No.	Zinc Added Mg.	Zinc Recovered Mg. A Original	B Modified
1	0.1	0.03	0.10
2	0.2	0.09	0.17
3	0.3	0.12	0.28
4	0.5	0.33	0.47
5	1.0	0.65	0.98

Summary of Modified Method

The weighed material, if organic in nature, is oxidized with sulfuric acid, then with nitric acid, ashed, and the ash is repeatedly extracted with hot dilute hydrochloric acid. After filtration the combined extracts are evaporated to dryness. The residue is dissolved in 2 cc. concentrated hydrochloric acid and 50 cc. of distilled water. The copper is precipitated as the sulfide, and removed by filtration. The filtrate, containing the zinc, is boiled to expel the hydrogen sulfide, cooled, neutralized with ammonium hydroxide and treated with 10 cc. of 50 per cent citric acid. The resulting solution is again heated to boiling and, if no calcium citrate separates, small quantities of calcium carbonate are added until a precipitate of about 1 g. of calcium citrate is formed. A rapid stream of hydrogen sulfide is then passed through the liquid until the latter has cooled. The flask is allowed to stand for several hours, part of the time on a water bath, until the supernatant liquid is clear. The precipitate is collected on a filter, washed with 2 per cent ammonium thiocyanate, and dissolved on the filter paper with hot dilute hydrochloric acid, the filtrate being collected in the flask in which the precipitation occurred. The appearance of a reddish color due to ferric thiocyanate indicates the presence of iron, in which case the zinc should be reprecipitated. A turbidity due to colloidal sulfur may be dispelled by boiling the solution. If clear and colorless, the solution is ready for the turbidimetric comparison. For this purpose the solution or an aliquot portion is diluted with water to 45 cc. in a 50-cc. Nessler jar. Other Nessler jars are prepared, containing definite volumes of standard zinc solution (1 cc. = 0.1 mg. Zn), 3 cc. of concentrated hydrochloric acid, and distilled water to make 45 cc. It is important that the Nessler jar containing the unknown should have an equivalent volume of concentrated acid. Five cc. of potassium ferrocyanide solution (34.8 g. per liter) are then pipetted into each jar. The liquids are quickly mixed, and the turbidities are compared by viewing longitudinally when the jars are held over a sheet of fine print. More of the standard zinc solution may be added from a buret to the jar having a turbidity which approximates the turbidity of the unknown most closely, until the turbidities in the two jars are identical.[1]

Conclusion

In our hands the modified method has been found more satisfactory than any other method for the estimation of less than 5 mg. of zinc. Even with larger quantities, 10 to 20 mg., this procedure compares favorably with other standard methods.

Acknowledgment

Acknowledgment is due to Professor W. C. Rose of this laboratory for his helpful suggestions and advice.

Platinum Theft

The Sierra Magnesite Co., of Porterville, Cal., reports a platinum theft from its laboratories some time during the night of June 14, 1921. Three platinum crucibles, weighing as follows, were taken.

No.	Grams
1	12.100
2	12.328
3	14.307

In addition, one Palau crucible weighing 14.491 grams was taken.

Exports of cottonseed oil from the United States in May 1921 amounted to 18,947,796 lbs. valued at $1,332,165, as compared with 11,655,272 lbs. valued at $2,595,235 in May 1920. This is an increase of 62 per cent in quantity, but a decrease of 48 per cent in value. The total cottonseed oil shipments during the 11-month period ended May 1921 were 269,105,939 lbs. valued at $30,287,371, as compared with 148,127,351 lbs. valued at $33,652,238 for the same period in 1920. The consumption of cottonseed oil during May 1921 was 307,000 bbls., the largest for any month this season.

---

[1] Zinc borosilicate glassware should not be used in zinc determinations.

A Simple Method for the Determination of Vanadium in Ores and Metallurgical Products[1]

By R. B. Schaal

FIRTH-STERLING STEEL CO., MCKEESPORT, PENNSYLVANIA

So many methods have been proposed for the determination of vanadium, that some excuse seems required for the publication of further material on this subject. This excuse is more than supplied by results returned to us on the analysis of a standard sample of high speed steel, which was submitted to three commercial and five works laboratories. The true vanadium content of the steel was 1.53 per cent. Results obtained by these laboratories varied between 0.86 and 1.74 per cent.

Previous to this time a modification of Johnson's method had been used at this works for the determination, but during the investigation of the standard sample we became convinced that our results were uniformly low, as much as 0.10 per cent on a 1.50 per cent sample. The present method is believed to meet all the requirements of accuracy, speed, ease of execution, and economy so necessary for routine and general use.

THEORETICAL AND PRACTICAL CONSIDERATIONS

The method depends upon the reduction of vanadic acid, by prolonged boiling with strong hydrochloric acid, to the tetravalent condition, and subsequent reoxidation with a suitable solution of potassium permanganate to the pentavalent state. The reactions involved are well known, and may be stated as follows:

$$V_2O_5 + 2\,HCl = V_2O_4 + H_2O + Cl_2 \qquad (1)$$

The reaction is completely displaced to the right by the removal of one of the reaction products, the free chlorine, by boiling.

$$5V_2O_4 + 2KMnO_4 + 6HCl = 5V_2O_5 + 2KCl + 2MnCl_2 + 3H_2O \qquad (2)$$

This reaction is found to run to completion with a sharp end-point, in a nearly neutral solution containing a suitable excess of ammonium phosphate, and admits of the presence of large amounts of iron, chromium, molybdenum, cobalt, nickel, uranium, titanium or zirconium, besides the amounts of manganese usually present in all samples.

The color of ferric chloride is destroyed by the ammonium phosphate.

Chromium, because of its deep green color, tends to obscure the end-point. This fact offers no difficulty to the chemist familiar with the determination of chromium by the ferrous sulfate-permanganate method, the end-point appearing as faint old rose reflections through the green. The use of an ordinary Mazda lamp behind a white screen clarifies the end-point to a remarkable degree, and the use of this device is recommended for all samples containing 3 per cent or more of chromium.

Molybdenum has been present in tests to the extent of 10 per cent, and apparently interferes in no appreciable manner. As the reduction of the vanadium by hydrochloric acid is selective with respect to molybdenum, this element remains in the oxidized state and is not affected by permanganate under the conditions obtaining in the titration.

Cobalt and nickel have been added in amounts up to 5 per cent of each, the only effect being the production of a slight green color.

Elements whose phosphates are insoluble, or partly so, under the given conditions, notably uranium, titanium, and zirconium, cloud the solution, but do not otherwise interfere. If present in appreciable amounts the precipitates may be removed by filtration.

By far the most important effect of the ammonium phosphate is that of converting any excess hydrochloric acid present, above the amount actually needed for the completion of the reaction, into the less highly ionized phosphoric acid, and thus minimizing the danger of action between the excess acid and the potassium permanganate. It is absolutely necessary that the directions for the final acidification of the solution be rigidly adhered to, if uniform results are to be expected. It should also be pointed out that excessive cold slows the reaction unnecessarily. If conducted at 20° C., however, the reaction proceeds with a rapidity which leaves nothing to be desired. The end-point does not disappear, as is the case in titrating cold sulfuric acid solutions, so slowly as to leave doubt as to the precise end of the reaction, but becomes permanent at once.

SOLUTION OF THE SAMPLE

STEEL—Weigh 2 g. of drillings or millings into a 500-cc. Erlenmeyer flask, cover with 60 cc. 1 : 1 hydrochloric acid, and heat until all action ceases. Remove from the hot plate, add 5 cc. strong nitric acid, and boil down to 10 cc.

ORES—Weigh 1 to 5 g., depending upon the vanadium content, into a 600-cc. beaker, digest with 60 cc. strong hydrochloric acid until the soluble portion is dissolved, add 5 cc. strong nitric acid and 2 cc. hydrofluoric acid, and evaporate to dryness.

FERROVANADIUM—Weigh out 0.5 g. of the 100-mesh powder into a 600-cc. beaker, cover with a watch glass, and add carefully 5 to 10 cc. strong nitric acid. Add 2 cc. of hydrofluoric acid, and heat. When violent action has ceased, add 40 cc. strong hydrochloric acid, and evaporate to dryness.

REDUCTION OF THE VANADIUM

To the sample prepared as in the foregoing paragraph, add 40 cc. strong hydrochloric acid, and evaporate to 10 cc. The nitric acid is thus completely expelled, and the vanadium partly reduced. Add 40 cc. more of the strong hydrochloric acid, and again evaporate to 10 cc. The vanadium is completely reduced, and the acidity greatly lessened. Add 60 cc. distilled water, and filter, using suction, through a 0.5-in. crushed, ashless, paper plug. Wash five times, using 15 cc. of cold distilled water for each washing. Any tungsten or tantalum which the sample contained is now removed. Transfer the clear filtrate to the original container, and add 60 cc. of a 15 per cent solution of ammonium phosphate. Add ammonia drop by drop until a bulky precipitate of ferricphosphate appears. Add, a few drops at a time, 1 : 1 hydrochloric acid until the precipitate just clears; then add 2 cc. in excess. In the case of ferrovanadium, where the color of large amounts of vanadium in the nearly neutral solution appears as a very deep orange color, reduce the color by adding 10 cc. 1 : 1 sulfuric acid. If the color still appears deep enough to obscure the end-point, add 10 cc. more of the ammonium phosphate and 10 cc. more 1 : 1 sulfuric acid.

Prepare a beaker (600-cc.) by etching a line at the 300-cc. mark. Just prior to titration transfer the solution to this vessel, and dilute to the mark.

TITRATION

Run in the standard potassium permanganate until two drops produce the first permanent pink. Blanks, made up to approximate as nearly as possible the material under

---

[1] Received March 18, 1921.

examination, are to be carried through parallel with each series of tests, and the amount of permanganate required by the blank is to be deducted from the amount required to titrate each sample. Blanks on some materials, especially those containing chromium, will be quite large, but they are accurate, and may be deducted with confidence.

STANDARD PERMANGANATE SOLUTION—The standard potassium permanganate solution is 0.0392156 N and is made up as follows:

Potassium permanganate	2.5 g.
Sodium or potassium hydroxide	5.0 g.
Distilled water to make	2000 cc.

To standardize this solution, weigh 0.1314 g. of Bureau of Standards sodium oxalate into a 400-cc. beaker, and cover with 200 cc. distilled water at 80° C. Add 10 cc. 1 : 1 sulfuric acid, and titrate slowly with the permanganate solution until the further addition of a single drop produces a faint permanent pink. Match this color in another beaker containing the same amounts of water and acid. Deduct the amount of permanganate needed to produce the end-point from that used in the titration of the oxalate. The result should be exactly 50 cc. If necessary, adjust the solution and re-standardize. One cc. of this solution is equal to exactly 0.002 g. of vanadium.

The author has little confidence in the so-called "practical test" method of standardization, except as it is used in conjunction with theoretical values. If results and theory do not agree, something, it would seem, is decidedly wrong with either the process or the standard used. We believe the standardization with sodium oxalate establishes with certainty the vanadium value of the permanganate. We are, however, careful to run, parallel with each series of tests, a standard sample, as a check upon the work.

It may be said in conclusion, that a rigid comparison of the new method with that of Blair, as modified by the American Vanadium Co.,[1] with Cain's phosphomolybdate method, and with the method of the Bureau of Standards, brings out an excellent agreement. In the particular case of the high-speed steel mentioned in the introduction the new method gives 1.53 to 1.55 per cent vanadium, and for the Government No. 50 Standard (0.756 per cent), 0.75 to 0.77 even with ordinary care. The blank, in these instances, was found to be quite high, from 1.9 to 2.0 cc.

[1] See Scott, "Standard Methods of Chemical Analysis," p. 273.

The Gold Number of Commercial Gelatins[1,2,3]

By **Felix A. Elliott and S. E. Sheppard**

Eastman Kodak Co., Rochester, N. Y.

As part of an inquiry into the physical and chemical properties of gelatins it was of interest to determine the extent to which gelatins could be classified by the variation of their gold numbers.

Zsigmondy[4] has defined the gold number of colloids as the number of milligrams of colloid necessary just to prevent the precipitation of 10 cc. of standard gold solution by 1 cc. of 10 per cent sodium chloride solution.

Preparation of Gold Hydrosol

A well-prepared gold solution should not appear turbid in reflected or transmitted light and should appear deep red in a thickness of 6 to 7 cm. It will withstand heating to boiling without precipitation. A turbidity noticed in direct reflected light is caused by particles larger than the average and indicates an inhomogeneity of the solution. Under the ultramicroscope a well-prepared solution exhibits a lively Brownian movement. The presence of an unresolvable hazy background indicates a considerable number of amicroscopic particles generally tolerated, but large yellow flashes in any great number across the field condemn the solution, as these are caused by the larger, undesirable gold particles.

Many methods are to be found in the literature on the preparation of gold solutions, but Zsigmondy's is very simple and satisfactory for this work. Very pure water is obtained by distilling water twice in a block tin still with a block tin coil condenser. Water with a conductivity of 1.2×10^{-6} was easily obtained and was satisfactory when used. The next precaution is to make all glassware to be used in the preparation chemically as well as physically clean. Zsigmondy insists on Jena resistance glass, but four of the leading American makes were used when properly cleaned, with excellent results. Three solutions are necessary: (1) 6 g. $AuCl_3.HCl.3H_2O$ dissolved and made up to one liter with conductivity water; (2) one liter of 0.18 N K_2CO_3 solution; and (3) a 0.3 per cent solution of formaldehyde.

According to Zsigmondy, 120 cc. of water prepared as above is heated and 2.5 cc. of gold chloride solution are added, then 3.5 cc. K_2CO_3 solution. This is stirred to insure uniformity and heated to 100° C. It is removed from the heater and 3 to 5 cc. of the formaldehyde solution are added with lively stirring.

A much smaller amount of formaldehyde solution was found sufficient. This had been observed by L. W. Eberlin in this laboratory in 1914, but it was not known whether this variation was due to uncertainty as to the strength of the formaldehyde. The more recent work has shown that the amount necessary is a function of the rate of addition (roughly inversely proportional). If the formaldehyde is added (0.5 per cent solution) a drop at a time and well stirred after each addition, this procedure followed until the solution begins to show a faint red tinge, and the additions now made only after a further color change is no longer produced by the previous drop, a deep red and extremely clear solution will be obtained. This solution was made up in lots of 2 liters to insure maximum uniformity throughout many tests, and about 2 cc. of 0.3 per cent formaldehyde were used.

Preparation of Gelatin Solutions

So-called hard, medium, and soft gelatins were tested.

The solutions were all made up with conductivity water at 50° C., each being heated 4 hrs. to complete equilibrium. After slow cooling to 20° these solutions were diluted to 0.001 per cent. A series in four steps was formed and the gold hydrosol added, followed by the sodium chloride solution.

In Table I are shown representative data obtained with seventeen different commercial gelatins of the three classes on the market, soft, medium, and hard. The data for the five samples quoted are representative of the different classes. The two color changes under each concentration are, first, the immediate color and, second, that observed after 24 hrs.

---

[1] Received April 8, 1921.

[2] Published as Communication No. 118 from the Research Laboratory of the Eastman Kodak Company.

[3] This work was done in October 1917 and discontinued on account of the war.

[4] *Ann.*, **301** (1898), 29.

TABLE I

SAMPLE No.	MILLIGRAMS OF GELATIN USED 0.005	 0.015	 0.015	CHARACTER OF GELATIN
1	B-P	SP-P	VSP-P	Soft
2	B-P	V-P	VSP-P	Hard
4	B P	P-P	SP-P	Soft
6	B-P	B-P	P-P	Medium
9	BV-P	SP-P	VSP-P	Medium

B Blue, P Purple, SP Slightly Purple, R Red, BV Bluish Violet, VSP Very Slightly Purple, VLP Very Light Purple, V Violet.

The data showing the actual color changes with increasing concentrations for each sample, while interesting, are omitted to save space. The gelatins fell roughly into three classes. The first class had a gold number of 0.005 to 0.010 and contained Samples 1, 3, 9, and 17. Class 2 had a gold number of 0.010 to 0.015 and contained Samples 2, 4, 5, 7, 10, 11, 12, 13, 14, and 15. Class 3, with a number of about 0.015, was made up of Samples 6, 8, and 16.

TABLE II

(1 per cent solution, 4 hrs. at 50° C.)

Milligrams of gelatin[1]	0.55	0.40	0.35	0.30	0.15	0.10
Immediate color	LP	VLP	PV	VPV	B	B
Color after 24 hrs.[2]	LP	LP	LP	LP	B	PB

[1] The residual color, when different from that produced immediately after the addition of the sodium chloride solution, indicates that the precipitation equilibrium is reached slowly and that a fraction of the gold is protected before the precipitation is complete.

[2] Intervening concentrations of gelatin were tried but these data are omitted to save space. Only the concentrations are cited at which distinct color differences were observed.

It was, of course, known that there is not great precision in the differentiation between hard, medium, and soft gelatins even from the same maker, so that it was not surprising to find no agreement at all between numbers in Classes 1, 2, and 3, and numbers classed as hard, soft, and medium.

As this classification is too coarse to be of value, a more exact differentiation was sought. Preliminary work along this line showed that there are three factors to be controlled very carefully:

1—The amount and the degree of heating.

2—The concentration at which the gelatin solution is heated.

3—The time of aging, *i. e.*, the time the solution is allowed to stand after having been made.

Inasmuch as the mere classification is of little scientific interest consideration will be given only to the control and influence of these three factors.

For this part of the investigation, Sample 14, a granulated gelatin, was selected, thus insuring maximum uniformity and ease of working. Three widely separated concentrations were selected, and all experiments were made with solutions at these strengths, *viz.*, 1, 0.01, and 0.001 per cent. This range would bring out the effect of concentration on protective action as denoted by the gold number. Solutions at these three concentrations were made up in three different ways:

1—By making the solutions up directly without subsequent dilution, as 1 g. gelatin to 100 cc. solution for a 1 per cent solution, to be heated for 4 hrs. at 50° C. to establish equilibrium and cooled in a water bath at 20°, at which temperature all gold numbers were determined.

2—By making an original solution of 1 per cent, heating at 50° for 4 hrs., cooling and diluting to 0.01 and 0.001 per cent at 20°.

3—By making the original solution of 1 per cent at 50°, heating for 4 hrs., and making further dilutions of 0.01 and 0.001 per cent at 50°, with a further 2-hr. heating to equilibrium and cooling at 20°.

The results shown in the condensed Table III clearly indicate that the gold number decreases with decreasing concentrations, that is, the protective action of the gelatin increases with decreasing concentrations. This is in agreement with the work of W. Menz.[1] The protective action is not increased by a decrease in the *quantity* of gelatin, but as the concentration is lowered the state of division of the gelatin present is altered. At high concentrations there is a majority of large particles with some smaller particles also; at low concentrations, a majority of very fine particles and very few of the larger particles. According to Menz's theory the larger particles exert very little, if any, protective action (*schutzwirkung*). His data and those here reported are in good agreement, tending to verify this theory. He further proved (and our ultramicroscopic observations corroborate him) that the amicrons actually do increase in proportion as the concentration is decreased. The slow increase in size of particles which occurs at room temperature when gelatin solutions "set" to a gel and even in the dilute solutions which do not congeal is due to a lag in adjustment of equilibrium which increases with dilution. Taking this into consideration, it is clear that the effect of aging is the agglomeration of amicrons forming larger particles, thus lowering the protective action. This accounts for a gold number of about 0.020 obtained for the 0.001 per cent solutions no matter how they had been prepared. The 0.001 per cent solutions had stood 2 days after having been made and had doubtless had time to agglomerate.

TABLE III—SUMMARY OF DATA

STRENGTH OF SOLUTION Per cent	GOLD NUMBER
Original	
1.0	0.15
0.01	0.020
0.001	*ca* 0.015
Diluted at 50°	
0.01	0.0075
0.001	0.02
Diluted at 20°	
0.01	0.0075
0.001	0.02

The temperature of dilution seems to have very little effect, at least within the range observed, and it is improbable that from 20° to 100° any difference would be noticed, because complete cooling to a uniform temperature of 20° would tend, at identical concentrations, to give similar distribution of small and large particles. If the gold numbers were determined at the dilution temperatures there would undoubtedly be a difference.

SUMMARY

1—Modifications of Zsigmondy's method for the preparation of deep red, highly homogeneous, gold hydrosols are given which make the preparation both easier and more certain.

2—Seventeen different gelatins of all grades and methods of manufacture were shown to differ but little in their protective action.

3—The classification thus made possible is too rough, and moreover does not bear any simple relation to those properties of chief interest to users of gelatins.

4—It has been shown that the gold number decreases as the concentration decreases.

5—It has been shown that the gold number increases the longer the gelatin solution stands or "ages" after it has been made.

6—The method of making the solutions was investigated, and the effect of cooking for different times and temperatures indicated.

7—The state of subdivision of gelatin solutions was very definitely indicated by these gold numbers and by ultramicroscopic observations. These solutions were shown to contain varying proportions of large and small particles, depending on the temperature at which they were in equilibrium, there being a predominance of large particles at lower temperatures.

---

[1] *Z. physik. Chem.*, **68** (1909), 129.

LABORATORY AND PLANT

Distillation Apparatus[1]

By Paul Gross and Alexander H. Wright

Chemical Laboratories of Trinity College, Durham, N. C., and Queens University, Kingston, Ontario

The different types of apparatus herein described have been devised from time to time to meet experimental situations arising in the course of the authors' work. For some of these no originality other than that of form is claimed. Their usefulness and simplicity, together with the general lack of knowledge concerning them, is deemed sufficient reason for recording them.

FRACTIONATING COLUMN

Anyone who has had to perform the frequent fractional distillations incident to the laboratory preparation of pure organic chemicals has felt the need for a fractionating column which was of good efficiency, and at the same time strong, simple of construction, easy to make or buy, and which could be quickly and thoroughly cleaned and set up. The still described below answers these requirements.

It consists of a straight tube A (Fig. 1) with a series of small bulbs sucked in on opposite sides, each pair of bulbs lying between the pair next above and below. The bulbs, being thin, permit of rapid heat exchange with the air outside. Their large area, together with the baffling of the ascending vapors by the alternately projecting bulbs, brings about a thorough contact between the liquid as a thin film and the rising vapor. These provide the necessary conditions[2] for efficient separation.

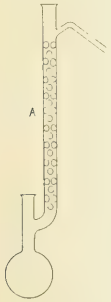


Fig. 1

If made of Pyrex glass and sealed to a flask as shown in Fig. 1, this makes a durable, efficient still. The thin bulbs are well protected. There is a free passageway down through the tube, which makes cleaning and draining easy, and there are no movable parts to lose or break. The cylindrical profile permits of fastening as with an ordinary straight glass tube, with clamps at appropriate points.[3] The symmetrical bulbs will stand the lowest pressure without breaking, thus making the still available for fractionations in vacuo.[4]

The efficiency of one of these columns (Table I) was determined by distilling a mixture of 50 g. each of purified benzene (b. p. 80.20° ± 0.05°, f. p. 5.50°) and toluene (b. p. 110.60° ± 0.05°) as recommended by Young.[5] The weights of the fractions between definite boiling temperatures were determined. The usual corrections for pressure and thermometers were made.

The data are for a tube of Pyrex glass 62 cm. long and 2 cm. in diameter, having 42 pairs of bulbs which approximated to three-fourths spheres of 1 cm. in diameter. This was sealed 2.3 cm. down the neck of a 250-cc. Pyrex distilling flask, and was provided with a delivery tube 4 cm. from the top. This represents an average column of this type which, though not the most efficient, is yet the handiest for all-round use.

Table I

Boiling Points of Fractions ° C.	Weight of Distillate Grams	Per cent of Total Distillate
80.2–83.2	4.587	4.6
83.2–86.2	22.590	27.3
86.2–89.2	10.883	38.2
89.2–92.3	7.322	45.6
92.3–95.4	6.086	51.8
95.4–98.5	4.877	56.8
98.5–101.6	3.257	60.1
101.6–104.6	1.931	62.1
104.6–107.6	5.356	67.4
107.6–110.0	5.425	72.8
110.0–110.6	5.656	78.6
110.6	17.192	96.1
110.6[1]	3.938	100.00
Total Weight	99.100	

[1] Residue remaining in column.

Comparison with Other Types of Columns

To obtain a more quantitative comparison between the various stills, each of the figures for the per cent of total distillate in Column 3 of Table I were plotted against the final temperature at which the fraction was collected. Curve B in Fig. 2 represents these results, while the other curves represent the results obtained by Young for two of his types of stillhead: Curve C, the rod and disk, and Curve A, the pear. The figures given are for stills of the same length as that used here.

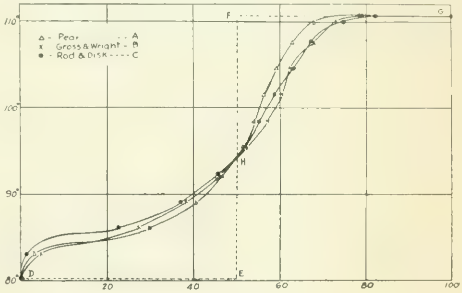


Fig. 2

The broken line DEHFG in Fig. 2 would represent a still which was 100 per cent efficient. That is, the curve would be identical with DEHFG, and the area between them zero. The benzene would all distil at 80.2°. The boiling point would then rise abruptly to 110.6° and the toluene would distil off. In a given case the area included between the first half of a curve and DEH plus that between HFG and the second half is a quantitative comparative measure of the still's efficiency. The smaller the areas the more efficient the still. The values of these areas from Fig. 2 are given (in arbitrary units) in Table II.

Table II

	Area under First Half	Area above Second Half	Total
Rod and Disk	2.6998	1.2027	3.9025
Gross and Wright	2.4421	1.1110	3.5531
Pear	2.3016	0.8120	3.1136

As the figures indicate, the efficiency of our column lies

---

[1] Received November 23, 1920.

[2] Young, "Fractional Distillation," 1903, 156, London.

[3] Compare Merriman, *J. Chem. Soc.*, **99** (1911), 994, who states, with reference to ordinary types of column, "a long fractionating column is a heavy piece of apparatus, and experience has shown that it is undesirable that any part of its weight should be borne by a clamp."

[4] Noyes and Skinner, *J. Am. Chem. Soc.*, **39** (1917), 2718, describe a fractionating column for distillation under diminished pressure, the principle of which is the same as that of the one described above.

[5] Young, *Loc. cit.*, p. 158. Some other more quantitative method of comparison such as that of Roberts, *Compt. rend.*, **168** (1919), 998, might well have been used here, but for the lack of the necessary data for the common forms of column with which it is desired to make comparison.

between that of the rod and disk and the pear of equal length. It must be remembered that the above column represents one for average use and is not the most efficient that could be made of this type. Also it is constructed of different glass.

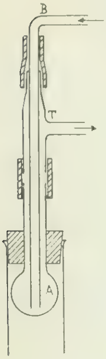


Fig. 3

This method of making a quantitative comparison by means of the areas under the curves is, as far as we know, given here for the first time, although it follows logically from Young's discussion.[1]

PROTECTION OF CORKS

It is very often necessary to fractionate liquids, the vapors of which either attack or exert a solvent action on cork or rubber stoppers. The usual methods of wrapping the stopper with tin or silver foil are only occasionally successful, and sometimes (as with high-boiling corrosive liquids like chloroacetic acid) fail utterly, necessitating recourse to expensive all-glass stills.

The device shown in Fig. 3 overcomes this difficulty. It consists of a small ball condenser which condenses the hot vapor and keeps it from reaching the stopper. If the bulb is blown from Pyrex tubing or other good grade of glass no fear need be entertained of its cracking on account of the temperature extremes to which it is subjected. It works admirably, for example, in protecting the lower stopper in the flask in such an apparatus as shown in Fig. 1.

MICRO-DISTILLING FLASK

Occasion often arises to distil and determine the boiling point of as little as from 0.5 to 2 cc. of liquid. If the liquid is pure the value can readily be determined by the submerged bulblet method.[2] In most cases, however, the liquid is a mixture, and it is necessary to separate the constituents and to learn the boiling points of the fractions to aid in their identification. The apparatus shown in Fig. 4 consists of a small bulb, A, about 1 cm. in diameter, with a side tube, B, sealed to it, which is the inner tube of the condenser C. In the top of A is a narrow well, about 0.5 cm. deep, made by softening the top of the bulb and pushing in with a charred wood sliver. In this well is put a drop of mercury about 1 mm. deep, into which dips the tip of a copper-constantin thermocouple.[3] The couple is best calibrated in the still by means of liquids of known boiling points.

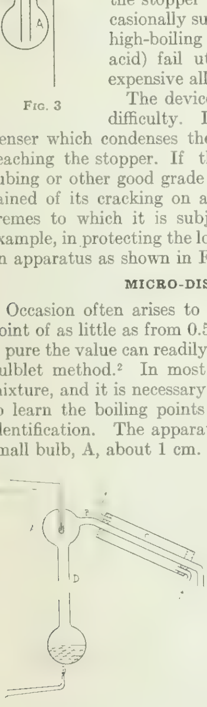


Fig. 4

RECEIVER FOR VACUUM FRACTIONATIONS

Many attempts have been made to solve the problem of changing receivers in a vacuum distillation without altering the pressure of the system. These are of two types: the first employing a by-pass controlled by stopcocks.[4] In the second type (Bruhl, Bredt, Gautier) the receivers are rotated (by means of a lubricated joint or connection) beneath the common spout delivering the distillate. Those of the first type have the disadvantage that the new receiver must be exhausted to the same pressure as the system, and they involve all the troubles attendant on the use of a number of stopcocks blown in a closed glass ring which is easily fractured.

The second type is more convenient, but at low pressures it is exceedingly difficult to keep the complicated moving joint or connection airtight and in proper alignment. In the receiver shown in Fig. 5 these objections are eliminated. In the desiccator, A, the revolving funnel, F, receives the distillate from G and is turned to the appropriate receiver from without by the strong magnet, M, acting on the iron wire armature, H. Tube C governs the vacuum.

Fig 5

VACUUM GAGE

Since for some substances the increase of vapor pressure with temperature is so slow, in a vacuum distillation a change of as much as a degree in boiling temperature may (especially at low pressures) result from a millimeter change in pressure. If the definition of the temperature is to be made to 0.1°, as is sometimes necessary in a fractional vacuum distillation, the pressure must be measured to 0.1 mm. The ordinary absolute manometer is not capable of this accuracy unless great pains are taken with its construction and filling, and special adjuncts (such as a vernier) are provided to aid the eye in estimating the tenths of a millimeter. The gage illustrated in Fig. 6 is a modified McLeod gage, but has several advantages (for the purpose in hand) over the usual forms of the latter. It is quick operating, direct reading, and simple in construction. The 10-cc. pipet A (closed at C) is calibrated so that volume v between C and H is one-eleventh of the volume V between C and K. At D a leveling tube F at least 90 cm. long is connected. The side tube B is 30 to 40 cm. long, and has a millimeter scale back of it whose 0 lies at H. The leveling tube F is filled with sufficient mercury to keep a seal when the mercury stands at the top of B. The system whose pressure is to be measured is attached to B. On raising F till the mercury stands at H in CH, the height HI in cm. is equal to the pressure in millimeters. By reading HI to 0.5 mm., the pressure is given to 0.05 mm.

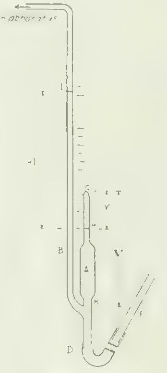


Fig. 6

The principle of the gage and its calibration is as follows: Let P be the pressure in the system to be measured. Before raising F this will also be the pressure in A. On raising F a volume of gas V is trapped in A, and its compression to volume v forces the mercury up in B to I. Let the pressure in v be p. This is greater than that in the system by the height HI cm. of mercury. Then by the gas laws:

---

[1] *Loc. cit.* 158

[2] Smith and Menzies, *J. Am. Chem. Soc.*, **32** (1910), 897.

[3] Constructed as recommended by White, *J. Am. Chem. Soc.*, **36** (1914), 1868, 2011, 2292, and Adams, *Ibid.*, **36** (1914), 72. Instead of using an elaborate potentiometer, if great accuracy is not desired, there may be used a millivoltmeter, or better, one of the numerous compact, portable instruments now available which utilize the potentiometer principle.

[4] Since writing this our attention has been called by Professor A. B. Lamb to a similar piece of apparatus described by Palomaa, *Chem.-Ztg.*, **1902**, 337. This method seems, however, to be generally unknown, although the only one which will accomplish the desired purpose simply and efficiently.

$$pv = PV$$
and $p = PV/v$
Also $HI = p - P$
$\therefore HI = P(V/v - 1)$
By the calibration $V/v = 11$
$\therefore HI = P(11 - 1)$
and $P = HI/10$

Therefore, the height HI, in centimeters, is equal to the pressure in millimeters. It is obvious that by changing the ratio V/v the sensitivity of the gage can be changed. Also in a given instrument two or more marks on CH with the accompanying knowledge of the volume ratios will increase the range of the gage. The one described will, however, be found the most convenient for general use, reading to 0.1 mm. or better, up to 30 mm., thus covering the range for most vacuum distillation.

The Consistency of Starch and Dextrin Pastes[1,2]

By Winslow H. Herschel and Carl Bergquist

U. S. Bureau of Standards, Washington, D. C.

This paper describes a preliminary investigation for the best method for determining the consistency of starch and dextrin pastes. While the results of tests are given, it is realized that they are approximate, and serve rather to show the value of the method employed than to indicate the exact qualities of the materials.

There are a great many substances which are not fluid enough to run through a viscometer under hydrostatic head, as in the well-known instruments of Saybolt and Engler, and which at the same time are not hard enough to be subjected to the Brinell test which is used for metals. Thus there are a variety of substances for which no standard method of measuring consistency is available, although many tests have been proposed. The term consistency is used to designate the degree of firmness or cohesion, and is applicable both to the viscosity of a liquid or to the plasticity of a plastic solid.

A number of kinds of penetrometer are in use for testing asphalt,[3] and other instruments which might be mentioned are the Legler consistometer[4] and the consistency tester of Hubbard and Pritchard.[5] It is doubtful, however, whether any of the above-mentioned instruments could be used to distinguish between a plastic and a viscous substance, a distinction which must be made if a clear idea of consistency is to be obtained.

THE DISTINCTION BETWEEN A PLASTIC AND A VISCOUS SUBSTANCE

The word plasticity is not always used with the same significance. According to Bingham,[6] plasticity is a measure of the consistency at a given time, while, as pointed out by Emley,[7] the plasticity of plasters and mortars depends upon the length of time during which they can be worked, and "consistency has little influence on plasticity." In this paper the usage of Bingham will be followed, and plasticity considered as independent of the change of consistency with time. Thus with plasticity, as with viscosity, a constant consistency during the time of test is assumed, although it is admitted that with some substances this assumption may be in error. It is known that lubricating greases may be forced through a capillary tube with greater ease the second time than the first, thus showing a softening of the grease as a result of a breaking down of the structure, and undoubtedly this same action may take place with other substances.

The difference between a viscous and a plastic substance may be seen in its behavior when subjected to successive pressures of increasing intensity. For a viscous liquid and a given capillary, the flow is proportional to the pressure. With a plastic substance (which may be considered a soft solid) the flow is proportional to the pressure in excess of a limiting amount p, obtained by graphical extrapolation. If it is assumed that

$$p = \frac{4lf}{d}$$

where f is the "yield shear value," and l and d are the length and diameter, respectively, of the capillary; and similarly

$$P = \frac{4l\,F}{d}$$

where F is the shear due to the total pressure P; then, in general, with a viscous liquid flow is proportional to F, and with a plastic substance flow is proportional to $F - f$.

The practical significance of the yield shear value for material such as paint, which is applied to a vertical surface, is shown by Table I, slightly modified from table given by Bingham and Green.[1]

TABLE I INFLUENCE OF CONSISTENCY UPON WORKING QUALITIES OF PAINTS, ACCORDING TO BINGHAM AND GREEN

RIGIDITY R	YIELD SHEAR VALUE f	WORKING QUALITY OF PAINT
Low	Low	Thin "runny" paint
High	Low	Thick runny paint. Will probably drag under the brush ("stringy" paste)
Low	High	Will not run easily, nor will it offer much resistance to the brush
High	High	Will have good body and covering power, and easily "stay put"

The yield shear value is thus a measure of the ability of a substance to resist moderate forces, such as the force of gravity, and adhere to a vertical surface where a liquid, even when very viscous, would gradually trickle down. Rigidity is the term proposed by Bingham for the property of a plastic solid which corresponds to the viscosity of a liquid; the reciprocal of rigidity is known as the mobility.

When there is at least a possibility that the substances to be investigated may be plastic, it is necessary to use a plastometer in which the rate of shear may be varied. This excludes from consideration most forms of viscometer, and leaves the choice of an instrument to be made between the variable pressure capillary instrument of Bingham, and some form of rotating instrument, such as those of MacMichael,[2] Doolittle,[3] Hayes and Lewis,[4] and Stormer,[5] in which the speed may be changed. Since only in the case of the Bingham instrument has the attempt been made to express R and f in c. g. s. units, this instrument was adopted for the tests to be described, as offering the most completely developed method of measuring plasticity.

---

[1] Received March 10, 1921

[2] Published by permission of the Director of the Bureau of Standards.

[3] See, for example, Herbert Abraham, "Asphalts and Allied Substances," **1918**, 480. The Dow penetrometer, supplied with a disk instead of a needle, is described in *Proc. Am. Soc. Test. Materials*, **6** (1906), 501.

[4] J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., I, 362.

[5] P. Hubbard and F. P. Pritchard, *Proc. Am. Soc. Test. Materials*, **17** (1917), II, 605.

[6] Bureau of Standards, *Scientific Paper* **278** (1916).

[7] *Ibid.*, *Technologic Paper* **169** (1920), 21.

[1] *Proc. Am. Soc. Test. Materials*, **19** (1919), II, 640.

[2] G. St. J. Perrott and R. Thiesen, THIS JOURNAL, **12** (1920), 324; W. H. Herschel, *Ibid.*, **12** (1920), 282.

[3] Seaton, Probeck and Sawyer, THIS JOURNAL, **9** (1917), 35.

[4] *Am. Soc. Mech. Eng.*, **38** (1916), 626.

[5] E. F. Higgins and E. C. Pitman, THIS JOURNAL, **12** (1920), 587.

THE QUANTITATIVE MEASUREMENT OF PLASTICITY

The fundamental equation for determining viscosity or rigidity by the capillary tube method is

$$R = \frac{\pi g d^4 (P - p)}{128\, q\, (l + \lambda)} - \frac{1.12\, \rho q}{8\pi (l + \lambda)} \qquad (1)$$

where R is the rigidity, ρ is the density in g. per cc., d and l are the diameter and length, respectively, of the capillary, in cm., λ is the "Couette correction" which must be added to the measured length of tube to get the effective length, q is the rate of flow in cc. per sec., P is the pressure causing flow, in g. per sq. cm.,[1] and g is the acceleration of gravity in cm. per sec.[2] = 981.

This equation does not apply to turbulent flow,[2] but it may be assumed that there is no turbulence if, with a very long capillary,

$$\frac{vd\,\rho}{R}$$

is less than 2000, or if with a capillary at least seven diameters in length, this ratio is less than 800. v is the velocity in centimeters per second. With liquids the yield shear value f equals zero, and the equation gives (instead of R) the viscosity μ in poises, the c. g. s. unit of absolute viscosity.

If the kinetic energy and Couette corrections are negligible, then from the relation between pressures and shears, Equation 1 may be reduced to

$$R = \frac{\pi g d^3 (F - f)}{32\, q} = \frac{C\ (P - p)}{q} \qquad (2)$$

where C is an instrumental constant which can be calculated from the dimensions of the capillary. This equation is however only an approximation, because, as shown by Green,[3] without any reference to any theory of shearing stresses,

$$\frac{pd}{l}$$

and consequently f, is only approximately constant with different capillaries.

Bingham[4] gives an equation equivalent to Equation 2 but derived by an entirely new method. Both methods are open to the same objection, that they are based on an assumed relation between pressures and shearing forces which cannot be justified, since p is always obtained by extrapolation from tests where there is considerable flow. We however accept 2 tentatively, as being the simplest empirical equation to give approximately the same values of R and f when tests are made in capillaries of different dimensions.

APPARATUS

The Bingham viscometer has been described in various papers,[5] and it is necessary here to refer only briefly to the parts of the apparatus which are used with the plastometer. It is essential for both instruments to have a supply of air under very constant pressure, a manometer for measuring this pressure, and a constant temperature bath with glass sides.

The apparatus used in the tests to be described was made in accordance with Fig. 1 of Bureau of Standards, *Scientific Paper* **278**, but experience in its use showed certain defects, and the instrument now in use at the Bureau of Standards was built from the design shown in Fig. 1 (this paper) in which the letters A to F and M have the same significance as in the *Scientific Paper* above referred to. It may be of interest to those desiring to build a plastometer to point out the difficulties experienced with the original instrument, which it was attempted to avoid in the new design.

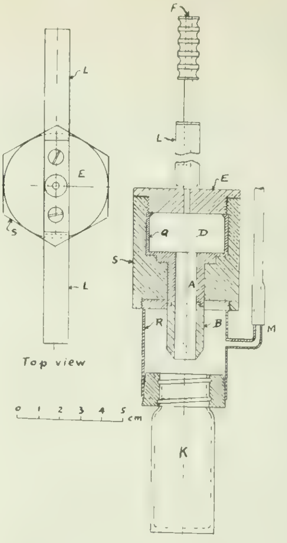


FIG. 1

1—Two supporting strips, L, were attached to the cover E, the strips also serving as a means of unscrewing the cover.

2—The plug, B, was made in two pieces so that the center of a long capillary could be accessible and it could therefore be more readily cemented into position. Care must be taken, however, that there is a tight joint between the two pieces.

3—The arrangement by which part B is held in position by the ring, Q, which is attached to the upper part of B, accomplishes two objects. The possibility of breaking the capillary with a wrench, as when B is screwed into the container, S, is avoided. There is also no danger of parts falling out when the instrument is taken apart, as would be the case if B were held in place by the tube R.

4—Leakage between R and S is avoided.

METHOD OF PROCEDURE

With the instrument as above described, it was found that it was convenient with certain capillaries, when working near room temperature, to bring the material to be tested to the proper temperature in an auxiliary bath, and then to pour it quickly into the plastometer. The instrument could be assembled so quickly that the error due to flow through the capillary before the air pressure was applied and the test started was negligible.

In the work with starches and dextrins a temperature of 25° ±0.5° C. was used in all cases, as this temperature makes unnecessary the use of ice in summer. The sample should stand at this temperature for several hours before being tested.

No capillary with a diameter less than 1 mm. should be used, since starch and dextrin always contain impurities which would clog a smaller tube, and the removal of these impurities would result in a new product. A range of diameters of 1 to 1.5 mm. has also the advantage of making it unnecessary to use very high pressures, while it permits pastes to be tested in the concentrations in which they are applied in practice. The length of capillary should be 25 to 40 mm., or at least 15 times the diameter in order that the Couette correction may be negligible. Several capillaries are needed, as the pastes will vary considerably in consistency.

---

[1] The calculation of P is simplified by tables given in a paper by Bingham and Green, *Proc. Am. Soc. Test. Materials*, **19** (1919), II, 653, and by E. C. Bingham in Bureau of Standards, *Scientific Paper* **298** (1917).

[2] W. H. Herschel, *Proc. Am. Soc. Test. Materials*, **17** (1917), II, 550.

[3] *Ibid.*, **20** (1920), II, 473.

[4] *Ibid.*, **20** (1920), II, 487.

[5] In addition to papers already mentioned, see E. C. Bingham, THIS JOURNAL, **6** (1914), 233; *Proc. Am. Soc. Test. Materials*, **18** (1918), II, 373.

If two samples are to be compared they should be treated exactly alike, be heated the same length of time at the same temperature, and left to stand the same length of time. This is especially necessary for starches. The sample is weighed, stirred with the proper amount of water in a wide-mouth, 4-oz. bottle, which has been provided with a cork stopper with a hole for a stirring rod, heated in a water bath to 85° C., and the temperature held constant for half an hour, while stirring from time to time. The samples are left to cool in the water bath over night, the best way being to put the bath into a constant temperature oven held at 25° C. This slow cooling will make the process similar to that in actual practice.

It is safest to start with the lowest pressure, as this will prevent undue agitation of the paste. After the fall in the hydrostatic head has been observed, the container is filled to the mark, the air pressure raised, and a new determination made.

EXPERIMENTAL RESULTS

Fig. 2 shows results obtained with starches, the rate of flow, q, being plotted against the pressure, P. It will be noted that the lower ends of the graphs are curved towards the left, this curvature having been noted by Bingham in his experiments with clay suspensions and attributed to seepage. This explanation does not appear applicable to our tests, as both a "soluble" dextrin and a practically insoluble starch, like pearl starch, show the curvature. Whatever the cause of curvature may be, the lower end of the graphs must be disregarded, and the straight upper portion extended (as shown by the dotted lines) to obtain values of p.

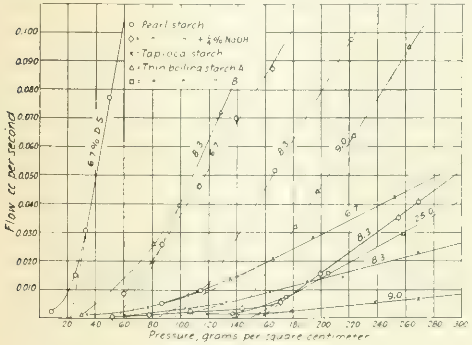


FIG. 2

For a given capillary there seems to be a concentration within certain limits most suitable for accurate results. If the paste is too thin, as with pearl starch containing 6.7 per cent dry solid, the flow increases too rapidly with an increase of pressure. If the paste is too thick and the flow is insufficient, as with tapioca starch with 9.0 per cent dry solid, it is very difficult to determine whether the experimentally determined points are on the straight or curved part of the graph. It appears that the best results are obtained when, at a pressure of 200 g. per sq. cm., the flow is between 0.020 and 0.045 cc. per sec.

Dextrins and gums came out in round, well-defined drops. In one case, borax gum B, at high pressure, the drops were long and stringy. With starch paste, no well-defined drops were observed, but the paste came out in chunks. On the other hand, when dextrin flowed into a receiving bottle filled with water, it did not appear in drops, but as a long unbroken string.

Fig. 3 is similar to Fig. 2, but shows the results obtained with dextrins and gums, which, it will be noted, have a much lower yield value than the starches. There is considerable difference in the shape of the graphs, some being perfectly straight like that for 60 per cent tapioca dextrin, and some curving so gradually and for so long a distance, like 30 per cent British gum A, that it is difficult to tell when the straight part of the graph is reached.

When more than one capillary is to be used, a sample large enough for runs in all the capillaries should be prepared. Each capillary should be mounted and ready, and runs with all capillaries at a given pressure should be made successively before changing to another pressure.

Table II shows values of R and f obtained from diagrams similar to Figs. 2 and 3, with the help of Equation 2. In some cases these are average values and do not agree exactly with the results of single tests as shown on the figures.

TABLE II—APPROXIMATE CONSISTENCY OF DEXTRINS, GUMS, AND STARCHES IN DYNES PER SQ. CM.

		Capillary 1		Capillary 2	
Kind	Concentration Per cent	Yield Shear Value f	Rigidity R	Yield Shear Value f	Rigidity R
		CORN DEXTRINS			
A	52.5	..	..	38	5.7
	55	..	..	477	7.0
	60	0	48.3	477	34.4
	62.5	328	61.4	477	67.4
	65.4	656	162.3	..	..
B	52.5	..	..	487	3.1
	55	..	..	524	5.7
	60	..	..	524	19.3
	62.5	347	21.5	(524)	(90.1)
	64.5	1030	48.3	..	..
	66.7	1930	135.0	..	..
C	52.5	..	..	114	4.4
	55	..	..	200	8.1
	60	..	..	692	41.9
D	52.5	..	..	38	4.3
	55	..	..	229	6.6
	60	..	..	1020	18.5
E	47.8	675	17.9	..	..
	50.0	732	185.2	..	..
	52.6	3300	303.0	..	..
		TAPIOCA DEXTRINS			
A	55	..	..	0	5.6
	60	..	..	19	15.4
	62.5	..	..	830	17.4
B	55	..	..	19	4.4
	60	..	..	258	10.0
C	55	..	..	76	5.1
D	60	..	..	19	13.3
		BRITISH GUMS			
A	30	..	..	982	2.8
	33.3	375	12.1	1125	6.2
	36.4	488	24.6	(1268)	(15.5)
	40.2	1160	41.7	..	..
B	25	..	..	715	4.8
	27.5	..	..	858	7.0
	30	..	..	(1030)	(20.5)
C	22.2	13	2.8	258	1.8
	25	656	4.3	792	6.5
	28.7	1010	18.2	..	..
		BORAX GUMS			
A	35	..	..	57	2.0
	40	75	9.6	458	5.1
	45	281	30.6	820	20.9
	50	281	196.0	..	..
B	16.7	..	..	1025	2.7
	20	94	24.6	1190	18.4
	22.5	1090	43.5	..	..
	25	1090	263.0	..	..
C	25	..	..	372	2.9
	26.7	..	..	897	6.8
	28.7	..	..	944	9.2
	33.3	..	..	1020	9.6
		STARCHES			
A, thin boiling	8.3	225	1.4	801	0.5
	9.0	525	5.5	1420	1.2
	11.1	1690	9.6	..	..
B, pearl	25	..	..	1400	4.5
	6.7	..	..	296	0.3
	8.3	1260	1.0	1030	1.4
	9.0	1820	4.4	..	..
	11.1	3320	5.4	..	..
Pearl + 0.25 NaOH	6.7	..	..	534	1.5
	8.3	..	..	1490	3.3
Tapioca starch	6.7	..	..	773	4.8
	8.3	1240	11.8	925	9.0
	9.0	1860	16.3	1210	24.6
	11.1	3040	28.8	..	..

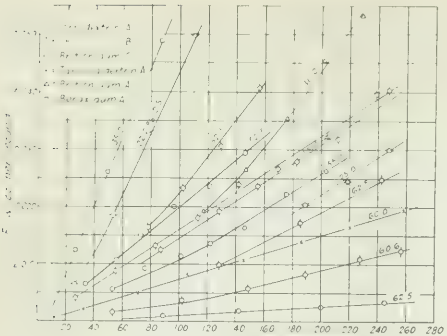


Fig. 3

The dimensions of the capillaries are given in Table III.

Table III—Dimensions and Constants of Capillaries

Capillary No.	Length Cm.	Diameter Minor Axis Cm	Diameter Major Axis Cm.	Calculated Diameter Cm.	Constant C of Equation 2	$\frac{l}{d}$
1	2 69	0 198	0.214	0 2058	0 01605	13.1
2	2 79	0.107	0.110	0 1085	0 00119	25.7

The variations in f in Table II may be partly due to error in measurement of capillaries, but it is believed that the main cause is the error in the graphical determination of p. The two capillaries differed too greatly in dimensions, so that suitable graphs could not be obtained by both capillaries for the same sample. Capillary 1 should have been smaller.

In Green's table the maximum change in value of

$$\frac{pd}{l}$$

due to change of capillary is only 14 per cent, which is less than with any sample in Table II. A slight difference in the location of the graph, owing to a different weighting of the various points, will cause a great variation in p, and hence in f. For this reason it is believed that most of the error in Table II is due to the attempt to locate the straight line necessary to find p, when all or nearly all of the points were in reality on the curved part of the graph. An additional source of error is the lack of accurate formulas.

Examination of Results with Capillary

When highly soluble dextrins are compared at the same concentration, 55 per cent, it is noticed first that tapioca dextrin A has a zero yield shear value and is consequently a viscous liquid. The rigidity or viscosity is 5.6 poises. The consistency of corn dextrins is shown in Table IV.

Table IV—Consistency of Corn Dextrins, 55 Per cent Dry Solid

Kind	Yield Shear Value	Rigidity
C	200	8.1
A	477	7.0
D	229	6.6
B	524	5.7

When the conversion takes place in the dextrinator, highly soluble compounds are first formed, as indicated by C in Table IV. The yield shear value is low and the rigidity high. When converted further, it is known that an insoluble compound begins to appear in A. This is indicated by the higher yield shear value. When still further converted to D, another change takes place, and the yield shear value, as well as the rigidity, decreases. This is well known in the actual use of these three products, from the fact that D gives a paste which has a smooth honey-like consistency.

By a simple efflux test it had been considered that C was the thinnest, A medium, and D the thickest. In the case of B the high yield shear value and low rigidity distinguish it from other products. If the yield shear value could be reduced, the product would have a consistency approaching that of tapioca dextrin. The subject requires further study.

In Table II the darker colored tapioca dextrins are viscous, and the lighter ones have a low yield shear value. British gums have a high yield shear value. It is interesting to see that British gum B, with about half the solubility of A, has about the same yield shear value but lower rigidity. This can be explained by the longer conversion of B which changes the insoluble part to compounds of less gelatinizing power, that is, lower yield shear value.

The difference between 25 per cent thin boiling starch B and British gum C is striking, the yield shear value for the former being 1400, while for the latter it is 792. This explains why B sets while C stays fluid.

A comparison of the 8.3 per cent starches is interesting. An addition of 0.25 per cent sodium hydroxide increases the yield shear value and more than doubles the rigidity, so that an alkaline starch will set harder and will have a better body than an acid starch. The thin boiling starch A will be a thin, fluid paste, in comparison, and tapioca starch will have the best body and the best covering power.

Conclusions

1—The Bingham and Green plastometer is the best type of instrument available for determining the consistency of plastic substances, although there is need of further improvements in method so that the values obtained may be independent of the dimensions of the capillary.

2—Adhesives of the concentration in which they are used are mostly plastic, but differences in yield shear value and rigidity of different samples of the same concentration are very striking and significant.

3—Many more results are necessary for a complete understanding of the different products, but it has been shown that the rigidity and yield shear value, as determined by the plastometer, will indicate the body, spreading power, and setting or gelatinizing power of starch and dextrin pastes.

Symposium on Chemistry in Coking and Gas Industries, New York Meeting, American Chemical Society

The fields of coking, gas works control and gas analysis will be discussed by various speakers at a symposium to be held on Thursday afternoon, September 8.

The two hours available for this program as a portion of the Division of Industrial and Engineering Chemistry will be devoted to four principal subjects: coke-oven problems, low temperature carbonization, gas works control, and gas analysis and its applications.

If the interest in the program and problems presented at the symposium seems to justify this, plans may be made for the formation of a regular section of the Society to deal with the chemistry of gases and fuels. It is emphasized by the committee in charge of the meeting, Messrs. C. H. Stone, H. E. Howe, and R. S. McBride, that the symposium will deal with the chemical problems rather than with engineering problems which are commonly considered at the meetings of the American Gas Association. However, it is hoped that the coöperation and attendance of all engineers as well as chemists will be had.

Further suggestions regarding speakers or subjects which receive attention at the meeting should be addressed to the secretary of the symposium, Mr. R. S. McBride, 610 Colorado Building, Washington, D. C. Those having articles which they desire to present at the September meeting on any phase of gas or fuel chemistry should send the abstract of their paper with title and author to H. E. Howe, Marine Biological Laboratory, Wood's Hole, Mass., on or before August 18, in order that their paper may be properly entered on the program. All individual papers on these subjects will be grouped together, probably for presentation on Friday morning following the symposium. The very brief time available for the symposium makes it impossible to include them in the Thursday afternoon session.

The Modulus of Hardness of Vulcanized Rubber[1]

By H. P. Gurney

Boston Belting Co., Boston, Massachusetts

To designate the firmness of vulcanized rubber, three words are used. These words with their dictionary definitions are:

1—Hardness: The cohesion of the particles on the surface of a body.

2—Density: The ratio of mass or quantity of matter to bulk or volume.

3—Plasticity: Plastic is defined as "capable of being molded, formed, or modeled, as clay or plaster."

The use of the words dense and density to convey the idea of hardness is a localism. Density possesses no necessary direct relation to firmness, although it often happens that materials of greater density are firmer than materials of lesser density. Plasticity (or plastometer followed by a number) is used as an inverse measure of hardness, particularly in paper mills. Vulcanized rubber possesses true plasticity only to a limited degree, although it exists to a considerable degree prior to vulcanization. Superposed upon, or associated with hardness in vulcanized rubber are such qualities as "flow," viscosity, hysteresis, internal friction, remanence, "comeback," and recoverance. It is very difficult to dissociate true hardness from these properties, and a certain residuum of these qualities inheres in all measurements of hardness.

The quickest and most natural way for the practical rubber worker to get an idea of the hardness of a piece of vulcanized rubber is to note the force required to indent to a certain degree, or the indentation produced by estimated equivalent muscular forces, using a sharp pencil point or a rounded key end. This method yields no definite figures.

Instruments for Measuring Hardness

In order to obtain some definite number for hardness and thereby to acquire an accurate method for the comparison of vulcanized rubbers, a number of instruments have been designed.

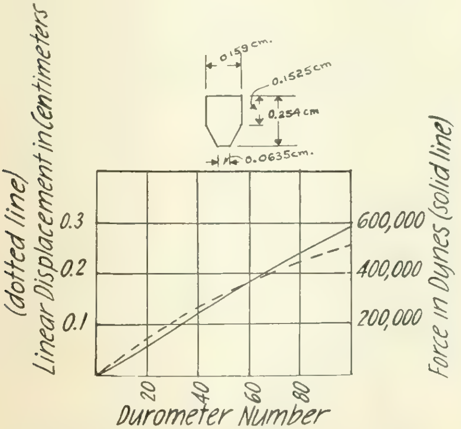


Fig. 1—Relation between Durometer Number and Force and Displacement

The spring type—With instruments of the spring type, the surface is indented by means of a point of a definite size and shape accompanied by a force which increases as the displacement of the point from its initial position increases. Surrounding the movable point and integral with the stationary part of the instrument, is a flattened collar which comes in contact with the rubber surface as the test is made. In Figs. 1 and 2 are shown the force and displacement curves with their relation to the scale readings of two instruments of the spring type which have been used for several years. The first of these instruments is a durometer. The scale ranges from 0 to 100, 0 being theoretically soft and 100 being theoretically hard. This instrument is small and extremely useful for quick and ready work. The other instrument is called a "densimeter," and the scale ranges from 0 soft to 1000 hard.

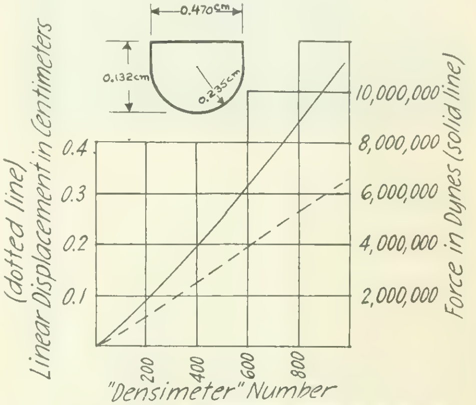


Fig. 2—Relation between Densimeter Number and Force and Displacement

The dead weight type—The marked disadvantage in the spring type of instrument lies in the fact that the readings vary with the personal equation of the one who uses it. To overcome this defect the dead weight type of apparatus was designed. In this type the depth of indentation, as in the spring type, is proportional to the reading, but the force of indentation, instead of varying with the hardness, is kept constant.

The most widely used instrument of the dead weight type is the plastometer. In this instrument, 0 is the plastometer number of an absolutely hard surface. As the softness increases, the plastometer number rises. For a point, either of two steel balls is used, one being 0.125 in. and the other 0.25 in. in diameter. The linear depth which the ball point presses into a flat horizontal surface is measured in units of 0.01 mm.

The order of operations prescribed in using this instrument is as follows:

1—The instrument is placed in a vertical position upon a horizontal, flat or curved surface of vulcanized rubber.

2—The ball point (usually the 0.125 in. diameter) is lowered until it rests firmly upon the surface of the vulcanized rubber. (The force with which it presses against the surface is about 85 g. of weight, which is due to spring tension within the dial of the instrument.)

3—The dial is adjusted to read 0.

4—A 1-kg. weight is lowered until it rests upon a shoulder just over and integral with the ball point.

5—After 60 sec. the dial of the plastometer is read.

---

[1] Presented in part before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

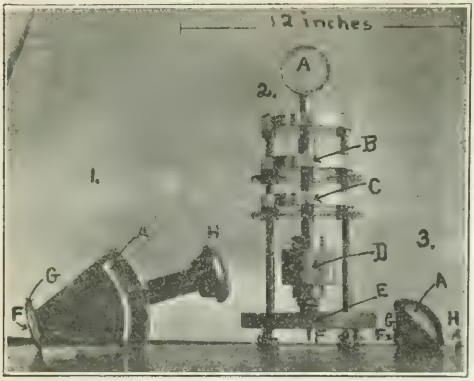


Fig. 3

1—Densimeter A—scale; F—movable point; G—fixed collar; H—operating handle.

2—Plastometer A—dial face; B—movable support for 1-kg weight; C—movable support, connected at rear with A; D—1-kg weight, which rests on either B or E; E—shoulder above ball point, F.

3—Durometer: A—scale; F—point; G—fixed collar; H—operating handle.

Owing to the fact that the initial downward force of the rod which connects the indicating dial with the ball point is 85 g. at 0 reading, the plastometer number may be defined as the depression increase, in 0.01 mm., produced by a sphere of the hardness of steel, when its force against a flat surface of vulcanized rubber is increased from 85 to 1085 g., and so maintained for 60 sec. This reading must be qualified by giving the diameter of the steel ball.

Fig. 3 shows the relative size of the plastometer (in the middle) with the densimeter and durometer on either side.

During the 60-sec. interval the reading on the plastometer dial gradually rises. Fig. 4 shows a series of seconds-plastometer plots upon a variety of vulcanized rubbers. There is no uniformity in the rate of rise, this depending upon the nature of the rubber compound and its heat treatment or "cure."

In order to get an insight into the nature of hardness, the plastometer was so modified that the force of depression upon the ball points could be varied from 0 up to 1000 g. (in c. g. s. units, 0 to 980,000 dynes) and the depth of depression noted for each force. The volume of the vulcanized rubber depressed or displaced downward was calculated, assuming it equal to the volume of the sphere which passes downward through the horizontal plane of the rubber surface. This volume can be calculated from the depression d in centimeters (the dial reading divided by 1000) and from the radius r of the steel sphere (0.3175 cm. for the 0.25-in. ball; 0.1587 cm. for the 0.125-in. ball). The formula to compute this volume in cc. is:

$$v = \pi d^2 (r - d/3)$$

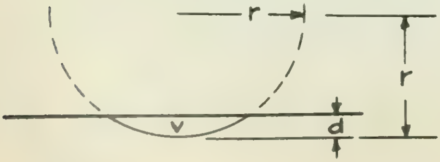


Fig. 5 exhibits the coincidence of the force-volume depression curves of two vulcanized rubber samples. Samples A and B were of plastometer readings 110 and 40, respectively, using 0.125-in. ball. These curves, like rubber stress-strain curves, are not exactly straight lines, but their curvature is slight except in the vicinity of the origin.

If a stress-strain curve were being dealt with, the modulus of elasticity would be defined as the ratio of stress to strain. In the case of vulcanized rubber, this ratio is by no means constant, although approximately so where the elongation does not exceed 100 per cent. The dimensions of the modulus of elasticity are the same as the dimensions of stress, namely,

$$\frac{\text{Mass}}{(\text{Length}) \times (\text{Time})^2}.$$

The modulus of hardness may be defined as the ratio of force to volume of depression. Its dimensions are:

$$\frac{(\text{Mass}) \times (\text{Length})}{(\text{Time})^2} \times \frac{1}{(\text{Length})^3} = \frac{\text{Mass}}{(\text{Length})^2 \times (\text{Time})^2}$$

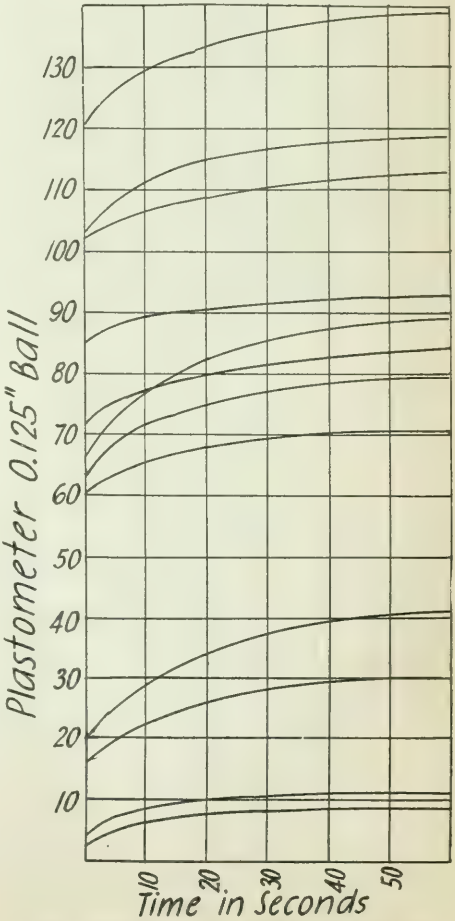


Fig. 4—Showing Rise of Plastometer Reading with Time

Hence it varies from the modulus of elasticity by the dimension:

$$\frac{1}{\text{Length}}$$

The dynes per cc. may be approximately estimated from the ordinary plastometer reading with the 0.125-in. ball by dividing (2.75×10^{12}) by the square of the plastometer number; though, owing to a possible variation in the initial force (which is about 85 g.), it is better to determine it from the force-volume depression curve of a specially designed apparatus. The dynes per cc. may be converted into other units:

Kg. per cc. by dividing by 980,000 (9.8×10^5).
Lbs. per cu. in. by dividing by 27,500 (2.75×10^4).
Tons per cu. in. by dividing by 55,000,000 (5.5×10^7).

Fig. 6 shows the relation between dynes per cc. plotted logarithmically and equivalent durometer, densimeter/10, 0.125-in. plastometer and 0.25-in. plastometer numbers. It follows from the formula $v = \pi d^2 (r - d/3)$ that the radius of the ball will vary almost inversely as the square of the depression, the hardness and force of depression being the same. Hence the readings with the 0.125-in. ball are $\sqrt{2}$ times the readings using the 0.25-in. ball. This ratio has been very carefully checked up, and it was the accuracy with which this checked up to 1.414 which became the inception of this investigation.

Variations in Apparent Hardness of Rubber

The apparent hardness of vulcanized rubber varies, not only with time, as previously pointed out in connection with the time-plastometer readings in Fig. 4, but with temperature and thickness of slab, if the slab rests upon a surface of a different hardness, as for example upon metal or glass.

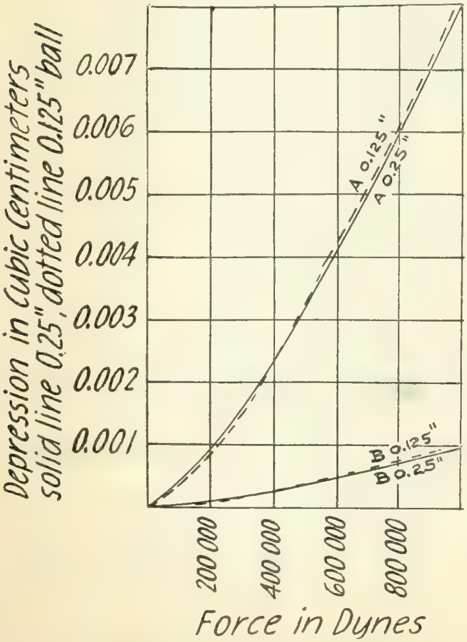


Fig. 5—Relation between Force and Volume of Depression Using 0.125- and 0.25-in. Ball on Two Vulcanized Rubber Surfaces, A and B

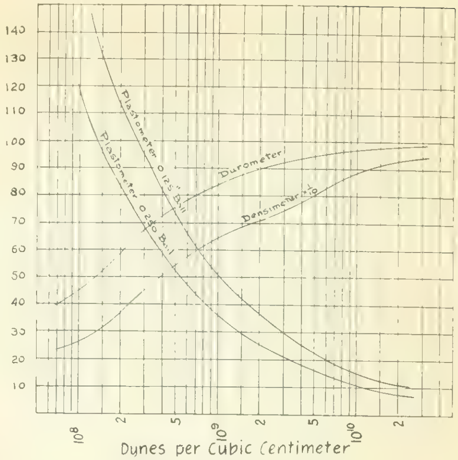


Fig. 6—Relation of Plastometer, Durometer and Densimeter Numbers to Absolute Hardness Units

Temperature—Fig. 7 shows the variation of hardness with temperature. Rubber compounds of a hardness of about 5×10^8 dynes per cc. (or about 80 plastometer) are apt to show less change with temperature than either harder or softer rubber compounds.

Thickness—Fig. 8 shows the effect of thickness upon apparent hardness, the vulcanized rubber slab being supported upon a glass plate (which, relatively to the rubber slabs, may be considered indefinitely hard). As the thickness increases, the hardness approaches asymptotically a limit, and this limit is attained sooner in hard, than in soft, slabs of vulcanized rubber.

Factors Determining Hardness of Vulcanized Rubber

In practice, it is found that vulcanized rubber increases appreciably in hardness from its time of fabrication. This varies considerably for different stocks and depends to a great extent upon the amount of free or uncombined sulfur. This hardening effect is greater the warmer the service temperature to which the vulcanized rubber is exposed.

Sulfur ratio—In general, greater hardness may be attained by increasing the ratio of sulfur to rubber in the compound, the proportion of mineral ingredients, the ratio of accelerator to sulfur, and (up to a certain point) the vulcanizing heat treatment (which may be defined by a time-temperature plot).

Fig. 9 exhibits the increase in hardness attainable through the use of a greater number of gram molecules of S_2 per gram molecule of $C_{10}H_{16}$. In the same plot also appears the increase in hardness due to a more extended heat treatment. The "vulcanizing units" referred to are the number of seconds that would be required to attain approximately equivalent physical and chemical properties if the vulcanization were carried on at a temperature of 150° C. Assuming that the rate or activity of vulcanization of rubber increases about 10 per cent for each ° C. of rise, then the vulcanizing units are equal to the duration of treatment multiplied by $1.1^{150-\theta}$, where θ is temperature and the activity at 150° C. is assumed at unity.

Heat treatment—Fig. 10 shows the effect of increasing heat treatment upon two series of experimental compounds of different rubber content (700 parts per 1000 by volume, dotted lines: 800 parts per 1000 by volume, solid lines).

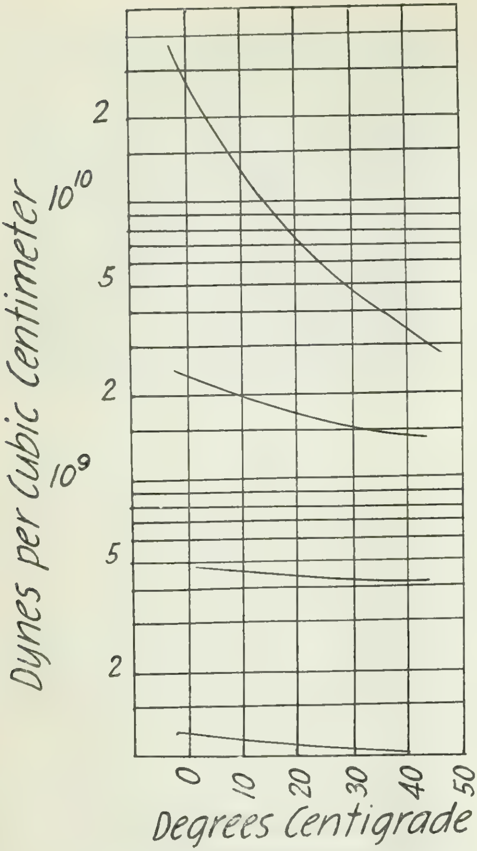


Fig. 7—Relation of Hardness to Temperature

The ratio of sulfur to rubber expressed in molecular proportion is 0.2 for the lower solid and dotted line, 0.3 for the middle solid and dotted lines, and 0.5 for the upper solid and dotted lines. In this plot, it will be noted that beyond a certain point, the vulcanized rubber softens. A solid line (800/1000 rubber) and a dotted line(700/1000 rubber) indicate that, as the rubber content increases, the loci of maximum hardness move parallel and toward a region of longer heat treatment.

These phenomena, particularly the reversal of the hardness curve and the effect of higher mineral content (lower rubber content) upon the hardness of vulcanized rubber, call for some discussion. It will be noted also that the reversal point is in the direction of greater duration of vulcanization for rubber compounds exhibiting greater maximum hardness. It has been conceded that in vulcanization two independent processes occur simultaneously:

1—A polymerization and resultant hardening, predominating in the initial stages of vulcanization.

2—A depolymerization which proceeds with accelerating speed.

Speculation concerning this phenomenon might seem to indicate that the hardening or polymerizing is due to the formation of a network by the adsorbed sulfur upon the polyprene molecules or colloidal aggregates. This network may conceivably possess a certain degree of rigidity. The same line of reasoning suggests that upon breakdown of this rigid network through the inward migration of the sulfur into the colloidal aggregate, the rigidity may decrease by a certain amount.

RUBBER CONTENT—Reference to Fig. 10 also shows that greater hardness is attained as the rubber content decreases. The reason for this lies only to a limited degree in the tendency for a more highly mineralized compound to vulcanize more rapidly. The principal cause for this lies in the fact that the distortion which the mineral matter is capable of assuming is absolutely negligible compared with the distortion which the vulcanized rubber is capable of assuming under equal stresses. The vulcanized rubber, considered entirely apart from the minerals embedded in and distributed throughout it, assumes practically the entire strain of distortion. The amount of distortion is affected by the size of the mineral particles, for the larger these are the greater the relative volume of vacuoles which are formed on either side of the particles in the lines of tensile stress.

Practical Application of Hardness Constant to Design of Rubber Covered Rolls

There is an application of the knowledge of the relation which exists between force and volume of depressed rubber. In the paper industry there is at present a considerable use of cylindrical hollow metal rolls uniformly covered by a thickness of vulcanized rubber of annular cross section. The hardness of vulcanized rubber determined under these conditions (the surface exhibiting a curved contour) is practically the same as when determined in the form of flat slabs. The theoretical deviation due to curvature would be extremely slight.

Under certain operating conditions, rubber covered metal rolls are run in pairs with axes parallel, the rolls being forced together by weights bearing at the journals. The force tending to squeeze the rolls together is varied according to the nature of the material being flattened out or calendered.

Let D be the outside diameter of either of two equal paired rolls (expressed in inches), of length L inches, and possessing a vulcanized rubber covering of hardness H lbs. per cu. in. It will be temporarily assumed that the metal portion of the

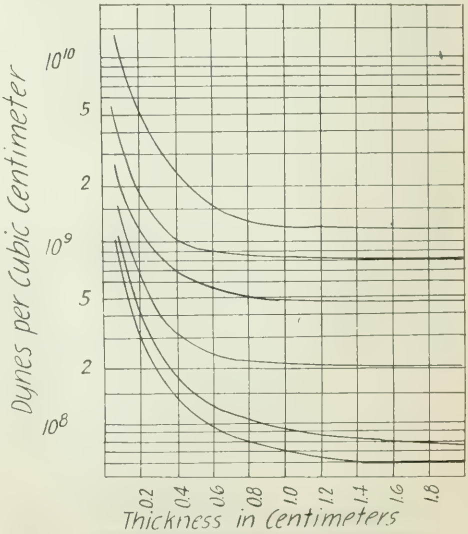


Fig. 8—Showing the Transmission of Hardness through Thin Layers

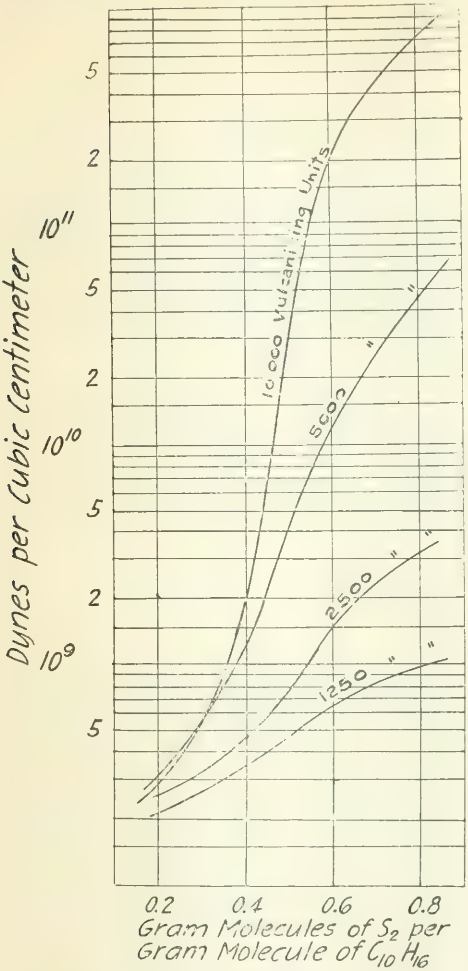


FIG. 9—EFFECT OF SULFUR-TO-RUBBER RATIO UPON HARDNESS

rolls is absolutely rigid (modulus of elasticity infinite). Let it be assumed that the surface of the vulcanized rubber is perfectly cylindrical, except at points of contact of the rolls, and that a total force, F, is compressing the rolls together, being uniformly distributed with respect to the length, L, that is, dF/dL is constant.

Fig. 11 illustrates diagrammatically how a flattening action resulting from the compressing force F will take place. There will be a maximum distortion of d in. of the surface of each roll along the line of intersection of the roll surface and a plane passing through the axes of the rolls. The width of flattened surface will obviously increase as d increases and may be designated by w (expressed in inches). Opposing and equal to the force of F pounds will be the pressures exerted at different points in the area of contact of length L and width w. The sum of all the products of the pressures into the infinitesimal areas dLdw over which they act is equal to the force F.

The knowledge of the value of H in absolute units gives us a means of predicting what these relations will be and is

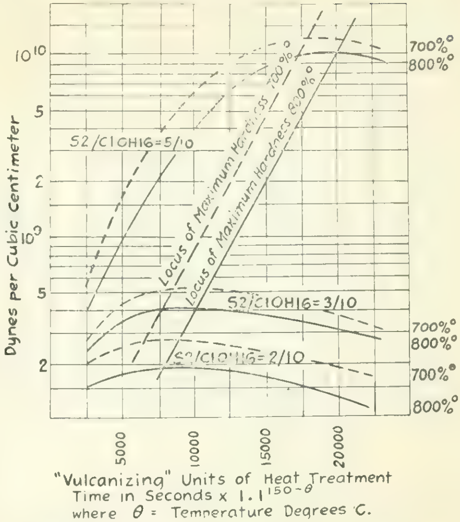


FIG. 10—RELATIONS BETWEEN HARDNESS, SULFUR TO RUBBER, EXTENT OF "CURE," AND PARTS OF RUBBER PER 1000 PARTS BY VOLUME

hence a fundamental constant to be dealt with, if calendering processes employing vulcanized rubber surfaces are ever to be put upon a rational scientific basis. Since it was immaterial in arriving at the constant H whether the radius of the sphere was 0.125-in. or 0.25-in., it will be assumed that for slight distortions the relation of force to volume depressed is independent of the exact shape of the volume displaced.

Then the maximum distortion d in inches will be:

$$d = \left[\frac{3F}{4\,H\,L\,\sqrt{D}} \right]^{2/3}$$

The maximum pressure in lbs. per sq. in. between the rolls will be:

$$Hd$$

and the average pressure will be:

$$^2/_3Hd$$

The width of contact w will be:

$$2\sqrt{Dd}$$

To work out an illustrative specific example, suppose the total force between two paired rolls is 3 tons (6000 lbs.), the length of the rolls is 150 in. and the diameter 20 in. Let the plastometer reading on the rolls be 70, using a 0.125-in. ball and waiting 60 sec. for reading. Let it be estimated that the

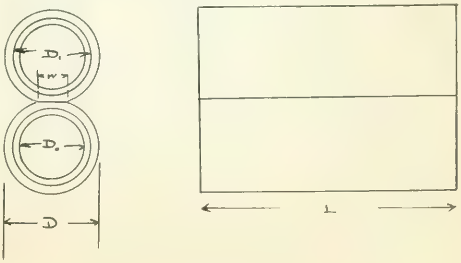


FIG. 11

0 second reading would have been about 60, corresponding to a hardness of 720,000,000 (7.2×10^8) dynes per cc., or (dividing by 27,500) 26,000 lbs. per cu. in. Substituting in the above formulas we get:

$$d = \left(\frac{3 \times 6000}{4 \times 26{,}000 \times 150\sqrt{20}}\right)^{2/3} = 0.004 \text{ in.}$$

$$Hd = 26{,}000 \times 0.004 = 104 \text{ lbs. per sq. in.}$$

$$\tfrac{2}{3}\,Hd = \tfrac{2}{3} \times 26{,}000 \times 0.004 = 70 \text{ lbs. per sq. in.}$$

$$2\sqrt{Dd} = 2\sqrt{20 \times 0.004} = 0.56 \text{ in.}$$

If the force be increased 8-fold, the depression d will be increased 4-fold to 0.016 in., hence the maximum pressure will be increased 4-fold, while the width of contact will double.

In the above, it has been assumed that the metal body or roll is absolutely rigid. Such cannot be the case. Assuming the load to be distributed uniformly, the deflection midway between the ends (at 1/2L) can be expressed in terms of the total force F, the external diameter D, and the internal diameter D_0 of the metal portion, and E the modulus of elasticity of the metal (assume 30,000,000 lbs. per sq. in. for iron).

From applied mechanics the maximum deflection f is:

$$f = \frac{5}{384} \cdot \frac{F\,L^3}{EI}$$

where

$$I = \frac{\pi\,(D_1^4 - D_0^4)}{64}$$

To take a specific example, let D_1, $=18$ in., $D_0 = 14$ in. and let F be 3 and 24 tons.

If F is 3 tons or 6000 lbs:

$$f = \frac{5 \times 6000 \times 150 \times 150 \times 150 \times 64}{\pi \times 384 \times 30{,}000{,}000 \times (18^4 - 14^4)} = 0.0027$$

If F is 24 tons or 48,000 lbs.:

$$f = 8 \times 0.0027 = 0.022 \text{ in.}$$

In order to compensate for this deflection, as well as to vary the maximum pressure with respect to the length if the process warrants it, a crown or convex curvature is applied to the surface of the roll. This crown may be so designed that the pressure will be distributed in any predetermined manner.

Under these conditions, the relation between depression, force per unit length, and distance along the roll will not be constant. dF/dL cannot be considered constant, but will be determined by the equation:

$$4Hd^{3/2}\ \sqrt{D}\,dL = 3dF$$

In this equation d may vary. It would be necessary under such conditions to develop equations for the deflection of the metal body.

Enough has been adduced to show the value of a hardness constant and the possibilities of its application to the design of rubber-covered rolls.

The Examination of Sugar Crystals by Projection[1]

By George P. Meade

Central Control Laboratory, Cuban-American Sugar Co., Cardenas, Cuba

Daily samples of raw sugar from a number of factories are received at the laboratory for examination of various physical characteristics, among which size and regularity of crystal are important. For convenience in reporting the size to the factories a scale of ten is used, No. 1 being very small, No. 10 very large, and No. 5 the medium size desired. Examination under a small tripod lens (2.5 to 3 diameters) and comparison with photographic standards proved fairly reliable in the hands of a trained observer, but the method was tedious and hard on the eyes, and did not admit of ready use by different operators. A method was needed which would be rapid, simple, and accurate, which would give a magnification of at least ten diameters, and which at the same time would show a sufficiently large number of crystals at one time to be representative of the sample.

It occurred to the writer that magnification by projection would fulfil all of these requirements. The apparatus selected for the purpose is a Bausch & Lomb Balopticon, Model C, with lens of 8-in. focus, one and five-eighths-inch diameter projection lens, and 400-watt incandescent Mazda lamp. The Balopticon is fitted with a vertical attachment in order that the object to be projected may be placed in a horizontal position. Experiment has shown that the apparatus magnifies ten diameters when placed with the center line of the projection lens exactly 7 ft. from the screen. To cut off the greater portion of the daylight, a black curtain made in the form of a tube or tunnel, about 3 ft. across, is hung on a frame of light iron rods, with the screen at one end of the tube and the projection apparatus at the other. The curtain can be drawn back when the apparatus is not in use, leaving the greater portion of the table which the apparatus occupies free for other work.

A small amount of the sugar to be examined is placed in a 40-mm. petri dish, a few cubic centimeters of sugar-saturated alcohol are added, and the crystals are separated by rolling them gently under the finger. The dish is then placed on a metal stage on the horizontal condenser, and the image focused on the screen.

Various methods of comparison were tried, but the one described below proved the most satisfactory. The screen is a smooth plaque of plaster of Paris, about 18 in. square and 0.5 in. thick. On the surface of the screen are drawn five squares, 3.5 to 4 in. on a side, subdivided as described below, and arranged so as to be distributed over the circle of light thrown by the projection apparatus. The lowest square is subdivided into 4-mm. squares, the next square into 6-mm. squares, the middle square into 8-mm. squares, and the other two into 10-mm. and 12-mm. squares, respectively. As our No. 5 sugar is about 0.8 mm. on a side, these sets of squares represent the sizes 3, 4, 5, 6, and 7, allowing for the magnification, and cover practically all of the range of sugars we receive.

The observer compares the projected image of the sugar crystals with the variously sized sets of squares and determines which size the majority of the crystals most closely approximate. This he can easily do to the nearest whole number of our scale, which is the full accuracy required for the purposes of our control. The form and regularity of the crystals are also noted, and in case these are abnormal the fact is reported to the factories for correction.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

Licenses were granted during July for the importation of 253,687.4 lbs. of dyestuffs from Germany by the dye and chemical section, division of customs, of the Treasury Department, according to the monthly report of the American Dyes Institute. In the same month licenses were granted for the importation of 145,848 lbs. from Switzerland, and 21,232 from England. The only license granted for French dyestuffs was for 12 lbs. of Victoria green.

Modified Laboratory Apparatus[1]

By C. C. Kiplinger

Mt. Union College, Alliance, Ohio

AN IMPROVED BURET AND HOLDER

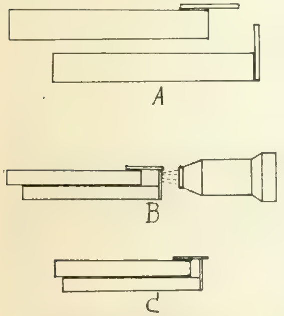
The common form of buret and buret holder possess three objectionable features, namely, masking of a part of the scale by the holder, difficulty of obtaining vertical adjustments, and last, the trouble and time required to manipulate the support. An ordinary buret with a thick-walled, funnel-shaped top, 4 cm. in diameter, hung in a slotted wood funnel support mounted on a tall stand, is free from the above disadvantages and need not cost more than the usual type.

Each opening of the wood funnel support has a slotted rubber crucible holder of the Bailey type cemented on it, so as to reduce to a minimum the danger of breaking the funnel tops. The slots must be wide enough to permit the insertion or removal of the burets without binding. With this device, the scale is always unobstructed over its entire length. Gravitation holds the tubes vertical and they may be instantly removed from the supports without fussing with springs or thumbscrews. The funnel tops obviously permit filling from stock bottles without the aid of auxiliary apparatus. Owing to the method of support, the tip may be moved over a certain portion of the table without disturbing the apparatus.

Because of the above advantages, this instrument insures greater ease of manipulation and increased speed in titrations.

A MODIFIED CELL FOR THE ULTRAMICROSCOPE

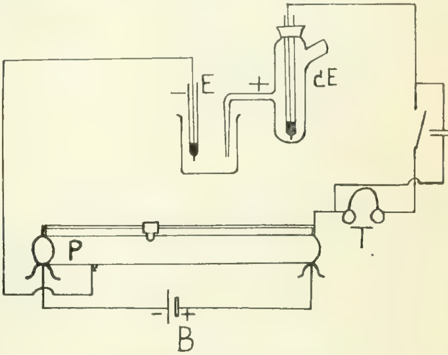
An ultramicroscope cell of simple construction, variable capacity and dissectible in type may be easily made of materials found in every laboratory. Two glass squares, 4 cm. on an edge, are cut from a good quality of plate glass 4 mm. thick. To the edge of one plate is cemented a strip of thin glass or clear mica 4 cm. long and 8 mm. wide, so that the edge of the strip extends 4 mm. above the surface of the plate. A similar strip 12 mm. wide is cemented to the top of the second plate so that it projects 4 mm. over the edge. Hence, when the latter plate is placed on the former and the two strips made contiguous, a long cell, 4 mm. by 4 mm. by 4 cm., and open at both ends, is formed, as shown in A and B in the figure. A spring clamp holds the two plates in position. The cell should be supported on a wire or cork stand which raises it above the stage so that the condensing objective of the ultramicroscope may be brought to the proper distance from the edge of the cell. The solution under examination is held in the cell by capillary attraction. The width of the cell can be changed to accommodate different quantities of liquid (C in the figure). Owing to its small size and the large ratio of length to width, convection currents are inappreciable. This cell is more easily constructed and cleaned than several others which the writer has used, and the fields obtained are excellent.



Cell for Ultramicroscope

TELEPHONE RECEIVERS FOR ELECTROMETRIC WORK

Two thousand ohm telephone receivers of the head-set type, such as are used for radio work, have been found of value in determining the null point in electrometric titrations, the writer preferring them to a galvanometer or a capillary electrometer in that they are dead beat and require no scale readings. This advantage permits the operator to confine his attention to the potentiometer and buret readings, thus decreasing the chance of error in the titration.



Telephones for Electrometric Work

The arrangement is as shown in the accompanying figure. The potentiometer P is arranged according to W. S. Hendrixson,[1] and the telephones (Murdock, No. 55, costing about five dollars are amply sensitive) are introduced into the circuit in place of a galvanometer, in series with a device for opening and closing the circuit, a telegraph key sufficing. The circuit is always kept open except when testing for the null point, which is indicated by the absence of sound in the receivers on tapping the key, hence the discharging of the electrode is reduced to a minimum. The high resistance of the receivers is especially favorable for hydrogen electrode use.

The following checks indicate the sensitivity of the method. Ten cc. of approximately 0.1 *N* $Fe(NH_4SO_4)_2.6H_2O$ were titrated against 0.1 *N* $K_2Cr_2O_7$.

Test	$K_2Cr_2O_7$ Cc.
1	10.00
2	9.90
3	9.90
4	9.84

A small fixed condenser, C, shunted around the key and receivers increases the sensibility of the device. The operator should assure himself that the key generates no local or contact currents on closing the circuit, which is done by removing the key from the circuit, then connecting it with the head set, which should yield no click on opening and closing the key. The high sensitivity and permanent adjustment of the receivers, combined with the ease of manipulation and low cost of installation, should commend them to the workers in this field. For very precise and delicate determinations the writer is installing vacuum tube amplifiers, which will greatly increase the cost of the apparatus, but which are unnecessary for ordinary work.

---

[1] Received April 11, 1921.

[1] *J. Am. Chem. Soc.*, **43** (1920), 14.

ADDRESSES AND CONTRIBUTED ARTICLES

Incendiaries in Modern Warfare[1,2]

By Arthur B. Ray

Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y.

(Concluded)

Part II—Incendiary Devices

It is beyond the scope of this article to go into great detail regarding the various mechanical devices which have been developed to carry incendiary materials and permit them to have an effective incendiary action. However, by means of general description and illustration the essential characteristics of all the types of devices developed by the warring nations will be given. The following classification of devices will be followed:

Small arms ammunition.
Shell.
Trench mortar projectiles.
Grenades and other hand devices.
Aircraft bombs.
Flame projectors.
Miscellaneous.

Small Arms Ammunition

Incendiary small arms ammunition, while carrying only a very small amount of material, has proved to be of the greatest value in effectively attacking highly flammable targets, such as aircraft, which are either filled with hydrogen or carry tanks of gasoline. Most of the incendiary ammunition is of the regular calibers and fits the standard machine guns, but a special size, 11 mm., which can carry more incendiary material has been successfully used and is highly recommended.

There are two classes of bullets which may have an incendiary effect—real incendiary bullets which may, or may not, begin to function before impact, and tracer incendiary bullets which begin to function at the instant of expulsion or shortly after and which, primarily intended as an aid in directing aim, may have considerable incendiary action, provided the target is struck before the bullet ceases to trace.

The types of incendiary materials used—white phosphorus and special oxidizing agent-combustible mixtures—have been previously discussed. As has been pointed out, the phosphorus is ignited by friction and the other mixtures are either ignited directly by the flare from the propellant or by a more sensitive primer which has been ignited by the propellant or by percussion.

The type of bullet which carries phosphorus is shown in Fig. 1.[3] When the bullet is fired the heat generated by friction quickly melts the fusible alloy from the vent and the molten phosphorus flows out and immediately ignites.

The regular caliber bullet carrying the tracer-incendiary mixture of barium peroxide and magnesium previously discussed is shown in Fig. 2. A 11-mm. bullet carrying the mixture of barium nitrate, magnesium, and charred linseed oil with an igniting composition of red lead and magnesium is shown in Fig. 3. This larger bullet is very effective, in fact, it is claimed that balloons can be ignited by it at 1600 yards. These three types of bullets were generally used.

The German perforating tracer-incendiary bullet, shown in Fig. 4, carried an incendiary material stated to consist of:

	Per cent
Strontium nitrate	75
Magnesium	13
Aluminium	3
Iron	6
Resinous material	3

The primer which was pressed in lightly was stated to consist of:

	Per cent
Potassium permanganate	55 to 58
Iron filings	45 to 42

The German armor-piercing incendiary bullet shown in Fig. 5 which proved to be especially effective against airplanes carrying protected gasoline tanks is interesting. The primer or igniting composition which is ignited upon impact consists of magnesium, potassium chlorate, and antimony sulfide. The incendiary charge consists of magnesium, aluminium, barium chlorate, sulfur, and a little nitrocellulose. The advantage of this bullet is that the burning composition in front of and around the armor-piercing core of steel is more likely to ignite gasoline, for example, from a perforated tank than if the composition were in a complete container which may be broken away from the bullet bodily on impact.

Shell

Shell designed to have an incendiary action, range in size from the small 37-mm. to the large 17.5-cm. shell. The smaller sizes were used with great success in attacking aircraft from the ground, and the larger calibers were used with moderate success against all sorts of flammable ground targets. There are tracer shell which have an incendiary action over a considerable portion of the trajectory and the incendiary shell proper which do not function as incendiary devices until the moment of bursting, when the incendiary material is ignited and usually expelled.

A common type of tracer-incendiary shell carrying the red lead and magnesium composition and primer is shown in Fig. 6. Shell of this type range in size from 37 mm. to 11.5 cm., but only the 75-mm. and 3-in. sizes were produced by the United States. These shell were used principally for balloon incendiary purposes. They are usually fitted with time fuses which are set to function considerably short of the target. The fuse charge ignites the primer which in turn ignites the incendiary mixture, and the incandescent products of the combustion are emitted from the shell through holes in the head. The smoke from this combustion leaves a definite trace of the projectile so that the laying of the piece may be corrected if the trajectory does not pass through the target. The hot gases have a very efficient incendiary action if the shell passes through the envelope of a balloon. These shell may begin to function when 50 yds. from the muzzle of the gun and continue this action for from 6 to 25 sec., depending upon their size.

A tracer incendiary shell which differs from the type just described in that it is base-opening is shown in Fig. 7. This type of shell, carrying a mixture of magnesium, barium nitrate, and binder, was used by British and Germans. Strontium nitrate was used sometimes to give a better tracing effect. The flash from the time fuse is transmitted through the central tube and ignites the small quantity of composition between the mill board washers. This fires the priming and the incendiary composition in the body. The base is blown out with the result that the flame is emitted through the base of the shell. This flame lasts for about 15 sec. and gives a tracing as well as incendiary effect.

Shell designed for incendiary effect alone may contain ther-

---

[1] Presented before the Division of Industrial Chemists and Chemical Engineers at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

[2] This article is published by permission of the Chief of the Chemical Warfare Service.

[3] Dimensions in this and other illustrations are given in millimeters except where otherwise indicated.

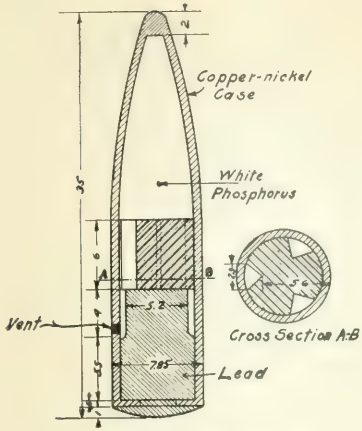


FIG 1—INCENDIARY BULLET, .303 INCH

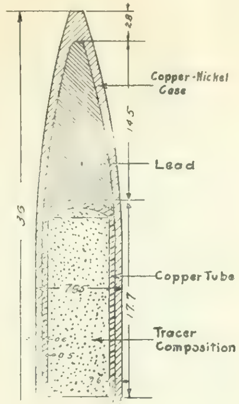


FIG 2 S.P.G TRACER BULLET, .303 INCH

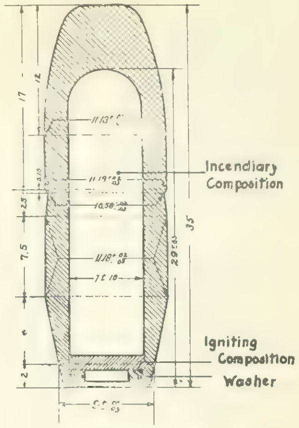


FIG 3—INCENDIARY BULLET, 11 MM.

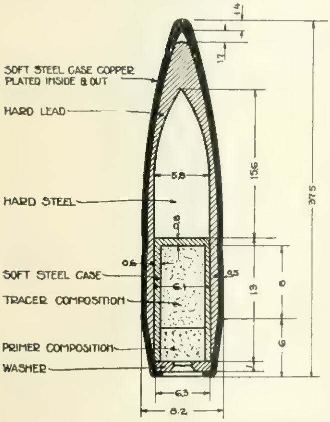


FIG. 4—PERFORATING AND TRACER BULLET USED IN AVIATION

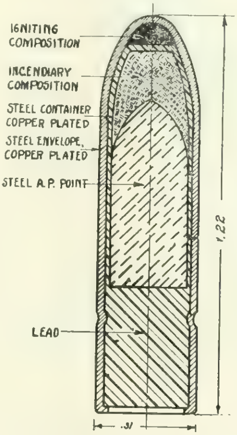


FIG 5—INCENDIARY ARMOUR-PIERCING BULLET

mite, special oxidizing agent-combustible mixtures, sodium, phosphorus, and flammable organic materials. The materials in some cases are present as small units which are ignited and scattered when the shell functions. In other cases the incendiary material is present as a mass which is expelled and more or less scattered when the shell functions. For an intensive incendiary action it is of course desirable to have as large a quantity of incendiary material as possible in one place, and for this reason extensive experiments were made with a type of shell which expelled but did not scatter its incendiary charge.

A typical small shell which carries thermite and an igniting and expelling charge of the potassium perchlorate-magnesium mixture known as ophorite is shown in Fig. 8. This type of shell acts as a shrapnel shell scattering the hot metal and slag produced by the thermite reaction and is said to have been particularly effective against aircraft. The time interval necessary for practically complete ignition of the thermite is obtained by the use of a beeswax plug between the igniting ophorite in the central tube and ophorite in the base. The thermite used may be the commercial product or a modified form containing, in some cases, manganese, copper, or lead oxide. It is usually compressed in the shells to prevent segregation. Our experiments with this type of shell, however, were not successful. We were unable to get complete combustion of the thermite or to prevent excessive scattering when the shell exploded. The incendiary action of the very finely divided and widely scattered material was not thought satisfactory, so a shell containing the incendiary material in definite units was experimented with.

A type of shell which contains units of thermite or an oxidizing agent-combustible mixture is shown in Fig. 9. The units held in perforated cases are ignited from the central tube and expelled from the front of the shell by the explosion of the charge in the base. The units are large enough to have considerable incendiary effect.

While this type of shell was not produced by the United States, it was extensively used by the other warring nations. The Germans used against aircraft a 7.7-cm. shell which on bursting scattered steel slugs and flaming incendiary units, called "flaming onions" by allied airmen. A 15-cm. German shell used against ground targets with little success contained twelve or more celluloid cylinders surrounded by white phosphorus and imbedded in paraffin, as shown in Fig. 10. A rather complicated Italian shell scattered 35 incendiary units when it functioned.

The largest incendiary shell used during the war was the 17.5-cm. German shell shown in Fig. 11. It contained, as shown, thermite and sodium, but despite its size was not especially effective.

A base-opening shell, which on functioning ignited and expelled a single large unit of incendiary material, was developed by us but not produced in quantity.

The general observation regarding incendiary shell is that the small caliber tracer-incendiary type was quite effective against aircraft but that the larger type designed for use against ground targets was not as successful, primarily because of the greater difficulty of igniting the type of ground targets in the war zone.

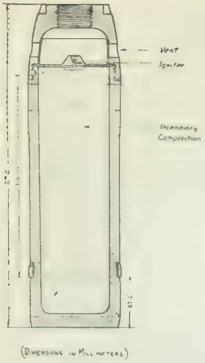


Fig. 6—75-Mm. Tracer Shell

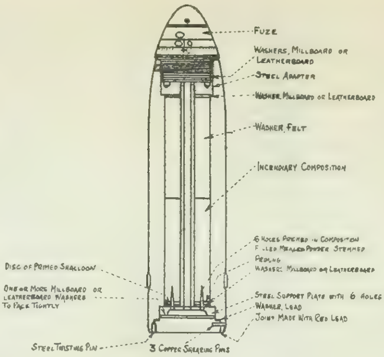

Fuze
Washers, Millboard or Leatherboard
Steel Adapter
Washer Millboard or Leatherboard
Washer, Felt
Incendiary Composition
6 Holes Pricked in Composition Filled Mealed Powder Stemmed
Pedling
Washer: Millboard or Leatherboard
Disc of Primed Shalloon
One or More Millboard or Leatherboard Washers To Pack Tightly
Steel Support Plate with 6 Holes
Washer, Lead
Joint Made With Red Lead
Steel Twisting Pin
3 Copper Shearing Pins

Fig 7—Incendiary-Tracer 75-Mm. Shell

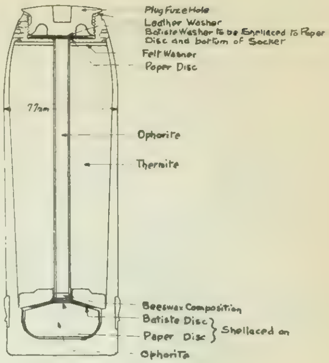


Fig. 8—77-Mm. Incendiary Shell

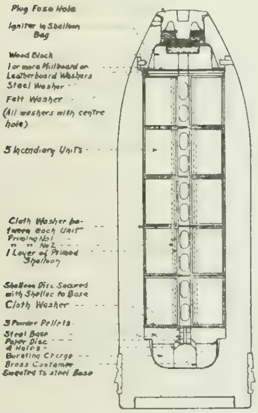


Fig. 9—6-In. (15.3-Cm.) Incendiary Shell

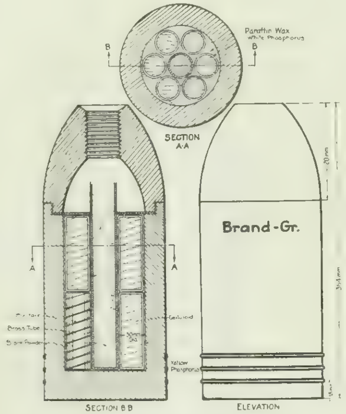


Fig. 10—15-Cm. Incendiary Shell

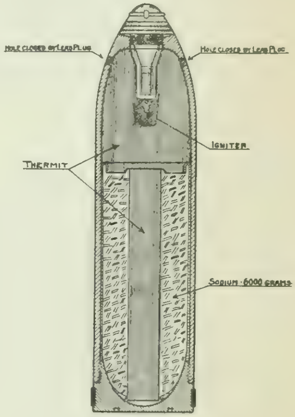


Fig. 11—17.5-Cm. Minenwerfer Incendiary Shell

Trench Mortar Projectiles

Trench mortar projectiles such as the 3-in. and 4-in. Stokes' bombs and the 8-in. Liven's drums were used to destroy grass, shrubbery, or camouflage which might act as a screen for enemy movements; to clean out woods; to demoralize the enemy during a gas projector attack, and to indicate the range in night projector attacks.

The Stokes' bombs loaded with phosphorus had little incendiary effect. When loaded with about 7.5 lbs. of slightly compressed thermite and the explosive igniter, "ophorite," and exploded in the air by time fuse arrangement they were more effective. Obviously the best results were obtained when the explosion took place near the target so that it was struck by the particles of hot or even molten metal and slag. Experimental work carried out at Hanlon Field, A. E. F., resulted in the development of an improved type of Stokes' bomb which scattered larger units of very hot metal. No other incendiary material has been satisfactorily employed in Stokes' bombs.

The 8-in. Liven's drum shown in Fig. 12 usually contained balls of cotton or jute waste and a special flammable liquid. The spontaneously flammable liquid previously discussed was developed primarily for use in these drums. The liquid generally used, however, consisted of a light and a heavy oil. The light oil is readily ignited by the flash from the explosive charge and the heavy oil gives the long burning desired. A mixture of light and heavy petroleum distillates gave satisfactory results. Soaking the cotton or jute balls in a chlorate solution and carefully drying in vacuum before putting them in the oil mixture caused them to burn with a fiercer flame when ignited. The units may also be soaked in molten "solid oil" and the oil allowed to solidify on them. This treatment results in more oil being carried with them when they are expelled.

These drums are fitted with an impact fuse which causes them to explode on landing. The oil saturated incendiary units are ignited by the flash from the explosive charge or take fire spontaneously if the special spontaneously flammable liquid is used and burn vigorously for sometime over an area approximately 50 yds. in diameter. The incendiary effect produced is good.

Grenades and Other Small Devices

While the use of incendiary grenades is limited, such armament is considered very valuable. Small portable incendiary devices can be used to set fire readily to flammable materials which it is desired to get rid of in either defensive or offensive operations. Several types of devices were used, such as real grenades filled with phosphorus or thermite, cans filled with flammable liquid and fitted with igniting and exploding devices, and paper or metal tubes filled with the oxidizing agent-combustible type of mixtures.

Grenades, usually made of sheet metal, containing white phosphorus and fitted with an exploding device, were of course used principally for producing smoke, but the burning phosphorus scattered by the explosion had some incendiary effect, particularly in dug-outs. The phosphorus-filled grenades were widely used by all armies, and their incendiary effect, although incidental, was not lost sight of.

Grenades containing thermite were used widely and proved to be very valuable for destroying or rendering useless guns and other material which had to be abandoned in retreat, for destroying airplanes which were forced to land in enemy territory, for igniting flammable liquids which had been thrown into dug-outs by any means or which had been sprayed over an objective by a flame projector. When aviators used these grenades to destroy airplanes after forced landing, one was placed on the gas tank, and one on delicate parts of the motor. The delayed action fuse allowed time for the men to place themselves at a safe distance. Automobiles and tractors which it was necessary to abandon were also easily destroyed in a similar manner. The breech mechanism of guns was effectively sealed by the molten iron produced by the thermite reaction.

A successful type of thermite grenade is shown in Fig. 13. In loading this grenade the thermite is moistened with sodium silicate, tamped into the sheet iron container, one end of which is open, and baked. The hole is bored in the center of the block and the cover is crimped on the container. The bag of aluminium-barium peroxide igniter from which the strands of quick match extend is inserted and the percussion firing plug put in place so that a piece of Bickford fuse in the plug is connected with the quick match. The charge of thermite weighs about 600 g.

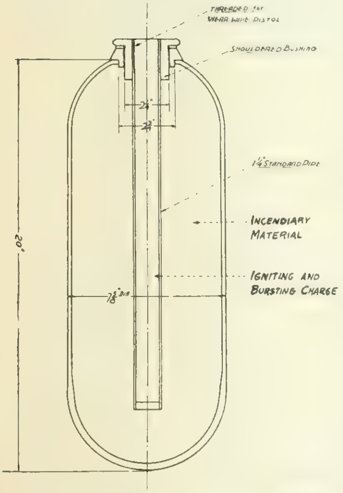


Fig. 12—Mark I Livens Incendiary Projectile

The Germans made use of small portable incendiary devices which usually consisted of tubes of metal or pasteboard filled with an oxidizing agent-combustible type of mixture and fitted with a friction igniting device. One kind of device contained 1670 g. of incendiary material of the following composition:

	Per cent
Potassium nitrate	62.5
Sulfur	27.0
Carbon	10.5

This material burns rapidly with a lively flame and gives off quantities of white smoke. The stated purpose of this device was to chase the enemy out of their shelters by a great development of flames and smoke. In actual practice it readily serves either as an incendiary or smoke-producing device, depending on circumstances. Its name, *Brand-rohren*, however, indicates the greater incendiary action. Other tubes of different sizes and containing different incendiary mixtures were used.

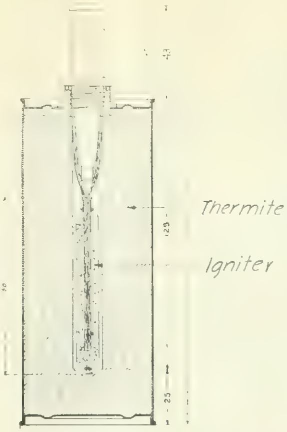


Fig. 13—Thermite Grenade

Some use was made by the French of a can which contained about 3 liters of a petroleum oil mixture and was fitted with a friction exploding and igniting device. In operation the device weighing about 7 lbs. was armed and thrown into trench or dug-out. It was reported to be quite effective.

With the idea of developing a device which would have both the advantages of the thermite grenade against metal and the advantages of the oil device against flammable material a combination thermite-solid oil grenade was experimented with. The thermite used in these experimental devices was found to be advantageously bound with celluloid—about 4 per cent by weight being used dissolved in a suitable solvent, such as acetone. Solid oil prepared as previously described was satisfactory. The arrangement of the materials is shown in Fig. 14. The grenade is fired by withdrawing the safety pin and releasing the bouchon firing handle as is done with all American grenades. The spit of the fuse ignites the booster which sets off the igniter and thermite in turn. The resulting molten iron and slag readily penetrates the grenade case, at the same time igniting the celluloid case and the solid oil. The mass burns with a large hot flame for about 4 min. This device was not produced because it was thought that the all-thermite grenade previously described would be of more value under the conditions then existing.

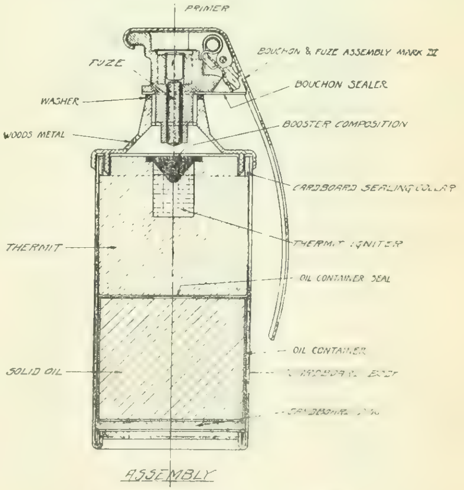


Fig 14 -Thermite-Solid Oil Grenade

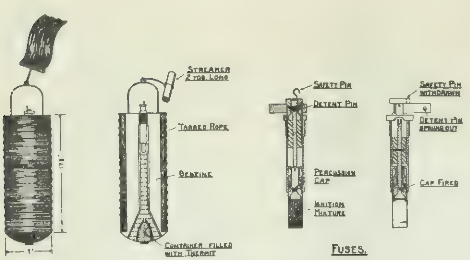


Fig. 15—Incendiary Zeppelin Bomb

Aircraft Bombs

It was early recognized that bombing by means of aircraft is of the greatest military importance, and it was also early recognized that incendiary bombs possessed great potential destructive power. It is interesting to recall that during the first raid over London on May 31, 1915, one German airship dropped four 200-lb. explosive bombs, twenty small explosive grenades, and ninety incendiary bombs. This armament was clearly designed to affect the maximum amount of damage to life and property in a populous town and indicates the importance attached to incendiary bombs. Later, incendiary bombs were extensively used by the allied airmen with considerable success.

The bombs developed and used since 1915 may be divided into three classes: (1) large bombs known as "intensive type" which burn practically *in situ*, (2) large bombs known as "scatter type" which on functioning scatter widely a number of incendiary units, and (3) small unit bombs which can literally be rained down upon a target. It is generally conceded that the scatter type is the least effective. Obviously the kind of bomb which can be most effectively used will depend upon the kind of target to be attacked. Grain crops, forests, and other relatively highly flammable targets which occupy a considerable area are best attacked by small unit or the scatter type bombs which permit a wide scattering of the incendiary materials. On the other hand, towns, factories, storehouses, ammunition depots, and similar targets are best attacked by intensive type bombs which burn with a large fierce flame.

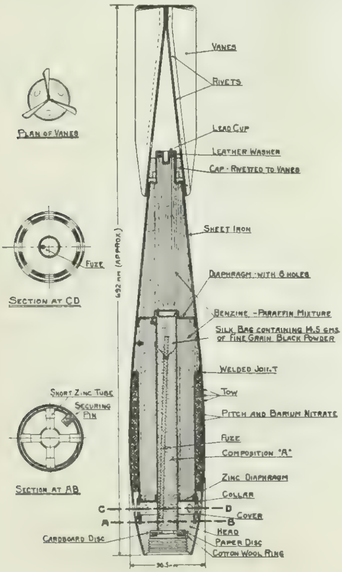


Fig 16—German Aeroplane Incendiary Bomb

The intensive type bombs developed comprise a large variety of models and carry practically all types of incendiary materials. The most satisfactory incendiary filling consists of thermite or other great heat evolving mixture and a larger amount of a highly flammable material. The first bombs dropped from German Zeppelins were of the intensive type. They weighed 20 lbs. each and, as shown in Fig. 15, contained benzine, thermite, and ignition mixture, and were wrapped with tow rope impregnated with tar and barium nitrate. A percussion fuse served to cause the first ignition. These rather crude bombs were dropped from airships only. A later type of bomb dropped from German airplanes as well as airships, shown in Fig. 16 weighed either 10 or 20 lbs. The main filling in these bombs was a pasty mixture of benzine and paraffin, or paraffin and potassium perchlorate. The central tube contained a mixture (composition "A") of aluminium, iron filings, and barium nitrate which was ignited on impact (fuse not shown) and served to heat up and ignite the other materials. The black powder explosion was intended to disrupt the sheet iron casing and scatter somewhat the incendiary materials. The bombs were wrapped with tow rope as shown and then shellacked over. They were extensively used and were fairly successful.

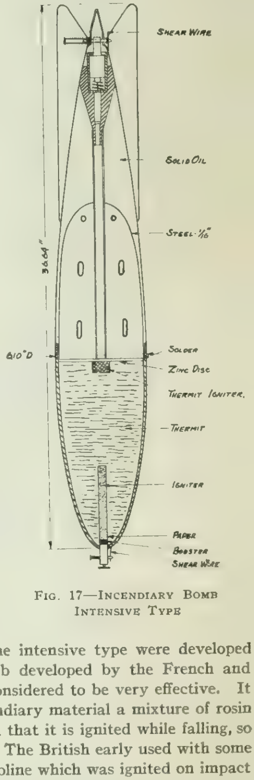


Fig. 17—Incendiary Bomb Intensive Type

A great many bombs of the intensive type were developed by the Allies. A 20-lb. bomb developed by the French and known as the "Chenard" is considered to be very effective. It contains as the principal incendiary material a mixture of rosin and celluloid, and is unique in that it is ignited while falling, so reaching the target in flames. The British early used with some success a bomb filled with gasoline which was ignited on impact by a Very cartridge. Other British bombs of this type filled with special oxidizing agent-combustible mixtures or, later, with thermite, were used, but the principal British bomb is the small unit bomb which will be described later.

A 50-lb. intensive type bomb was developed by us which contained, as shown in Fig. 17, thermite and solid oil as the principal incendiary materials, and had an impact ignition mechanism held in the nose or the tail of the bomb, or both. As shown in Fig. 18, the bombs consist of two main parts—the steel nose and the sheet zinc body with the sheet iron vanes attached. The thermite bound with sodium silicate as previously described may be baked in sheet iron cans which are then placed in the nose or it may be baked directly in the nose. The solid oil is run into the zinc body while warm and fluid and allowed to harden. To protect the thermite from the oil a zinc plate is

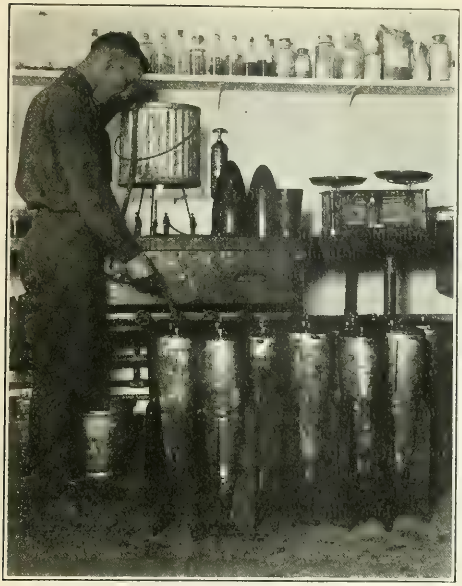


Fig. 18—American Experimental Intensive Type Bomb—Loading with Solid Oil

soldered over it. The body or rear casing is strengthened and the central tube held firmly in place by the steel cup, as shown in Fig. 17. Ignition may be effected by a black powder flash or by the bullet from the service cartridge. The arrangement of the ignition mixture, which is slightly compressed to prevent segregation, is shown. When the bomb functions on landing, the thermite, being first ignited, serves to burn through the casing, and the immense amount of heat liberated quickly melts, volatilizes to a certain extent, and ignites the oil which begins burning with a tremendous burst of flame which is most effective. The zinc casing is readily destroyed and the solid oil continues to melt and spread the conflagration. The expressed opinion of those who have witnessed these bombs in action is that the incendiary materials are highly efficient and that any further developments should be directed toward the mechanical improvement of the bomb.

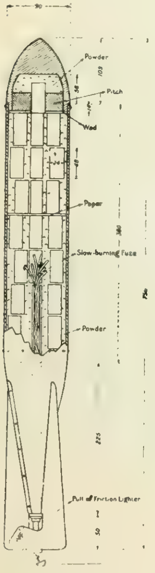


Fig. 19—Scatter Type German Incendiary Bomb

Many varieties of the "scatter type" bomb have been developed. A 40-lb. air burst bomb filled with white phosphorus was used by the British against observation balloons and ground targets. A rather inefficient 20-lb. bomb developed by the French functions on impact and ejects one or more ignited units of an incendiary material, consisting of cotton impregnated with a flammable liquid and a mixture of potassium perchlorate and paraffin. It is interesting to note that the igniting and explosive material in this bomb is a sulfur-bound thermite, which when ignited in a confined space acts as a mild explosive as well as a great heat producer. A 50-lb. scatter type bomb developed by us is identical with the intensive type as far as outside dimensions are concerned. It may contain units consisting of waste tied into balls and saturated with flammable liquid such as a mixture of crude turpentine and carbon disulfide. Or the units may consist of a core of solid oil held in a celluloid container or an oxidizing agent-combustible mixture, about which is wrapped waste impregnated with ammonium nitrate and coated over with a mixture of trinitrotoluene and naphthalene. The units are usually about 3 in. in diameter. When the bomb lands, ignition and ejection of the units are effected by an explosion of black powder in the nose. A simultaneous explosion of a smaller amount of powder in the rear disrupts the bomb casing and assists materially in the scattering of the units. While this type of bomb was developed it was not used because the small unit bombs or darts were considered more effective. A bomb similar to the one just described, in that balls of waste saturated with a flammable liquid were ignited and scattered, was developed by the Italians.

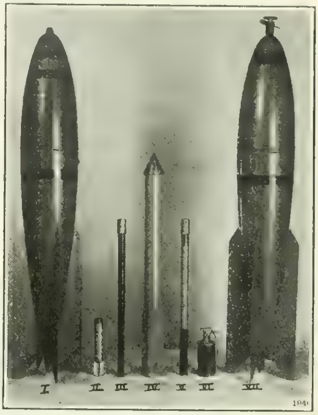


Fig. 20

I—American Intensive Type Incendiary Drop Bomb
II—British Small Unit Type Incendiary Drop Bomb
III, IV and V—American Small Unit Type Incendiary Drop Bombs
VI —American Thermite—Solid Oil Incendiary Grenade
VII—American Scatter Type Incendiary Dry Bomb

A late model bomb used by the Germans, shown in Fig. 19, was designed to burst in the air and scatter forty-six small incendiary units. These units consisted of perforated zinc cylinders filled with about 50 g. of a nitrate-sulfur-tar mixture which burned quickly with a small hot flame.

While these various scatter type bombs are fairly effective against readily flammable targets, it is generally believed that the more recently developed, small unit bombs can be used to a better advantage. The British originated the idea of dropping a large number of small unit bombs instead of one large scatter type bomb, and developed the 6.5-oz. bomb shown with American bombs in Fig. 20. In principle this little bomb follows that of a mortar and projectile complete. It carries a cartridge very much like a shotgun shell which on impact sets down on the striker point in the base of the body thus causing the functioning of the cap which simultaneously ejects the cartridge and causes ignition of the incendiary charge. This charge is the special flaming thermite previously described.

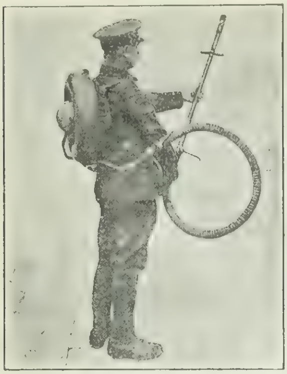


Fig 21—German "Wex" Portable Type Flame Projector

The little bombs are loaded into containers which are hung underneath the airplanes in such a manner that they may be released as desired. Each container may carry 144 or 272 bombs, depending upon its size. The number of these bombs which can be carried by one airplane runs from 860 carried by a De Haviland 4 up to 16,000 carried by a Handley-Page V type. It is apparent that by formation flying the bombs can literally be rained down upon a large area of target and practically cover it with a sheet of flame. And it is claimed by the British that since the terminal velocity of the bombs is such as to cause them to penetrate heavy roof constructions they can be used most effectively against towns and factories, preferably in conjunction with large, high-explosive bombs. There is some question, however, as to the real efficiency of the incendiary material employed.

Following the British idea we have developed two types of small bombs or darts, as they are called by us. One type intended primarily for use against crops and forests has no great penetrating power and burns with a very large flame. It carries the oxidizing agent-combustible mixture especially developed for it, which has been previously described, in an elongated 12-gage shotgun shell and functions on impact by reason of a simple firing device. The other type, intended primarily for use against building constructions, has sufficient penetrating power to pierce the roof, and carries a sufficient amount of incendiary material to be effective. The incendiary material is the efficient thermite-solid oil combination, previously discussed, held in a zinc container. Neither of these darts was produced in quantity. Both are shown in Fig. 20.

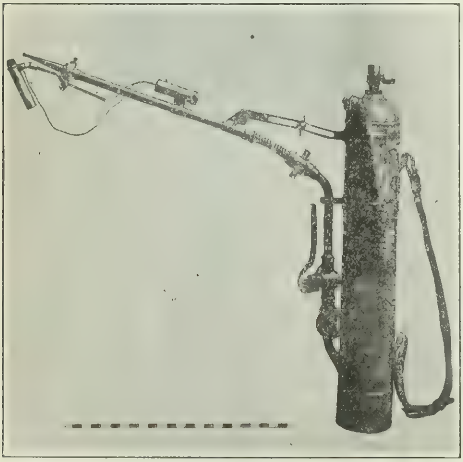


Fig. 22—Hay Flame Gun

Flame Projectors

Devices for projecting flaming liquids were originated by the Germans and used early in the war with considerable success, which was due, however, more to the demoralizing effect than to the actual destructive power. Flame projectors have since been developed by the Allies and used to some extent.

The principle of all flame projectors is the same. Usually a suitable flammable liquid contained in a metal reservoir of greater or less capacity is put under heavy pressure by a compressed gas in a steel cylinder connected to the reservoir, generally through a reducing valve designed to maintain a given pressure in the reservoir. The liquid is forced out of the reservoir through a pipe fitted with a valve and terminated by a nozzle of suitable diameter which directs the stream towards the enemy. The liquid is ignited either at the end of the nozzle by means of attached igniting devices, or, where it is projected on the earth, by means of incendiary grenades which are thrown into the area played upon by the stream.

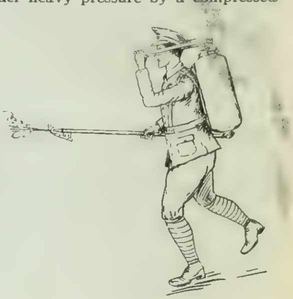


Fig. 23—"Lawrence" Portable Flame Projector

The flammable liquids and igniting devices used have been previously discussed.

The propellant gases generally used are nitrogen, hydrogen, carbon dioxide, and air, each of which have certain advantages and disadvantages. Absolutely dry carbon dioxide, owing to the fact that it can be readily liquefied and compressed into small volume, is recommended very strongly. Liquefied or compressed flammable hydrocarbon gases are unsatisfactory because of their physical characteristics. In some cases the gas is charged directly into the cylinder with the liquid, but this is not considered a satisfactory practice. The compressed gas is usually carried in a separate cylinder.

The pressures which it is possible to employ depend largely upon the diameter of the nozzle. The longest throw possible is desired, and the characteristics of the liquid, the diameter of the nozzle, and the pressure are all adjusted to this end. With a given liquid and size of nozzle the length of throw increases

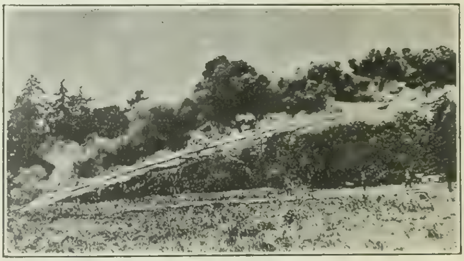


Fig 24—"Lawrence" Flame Projector Being Fired from Ground

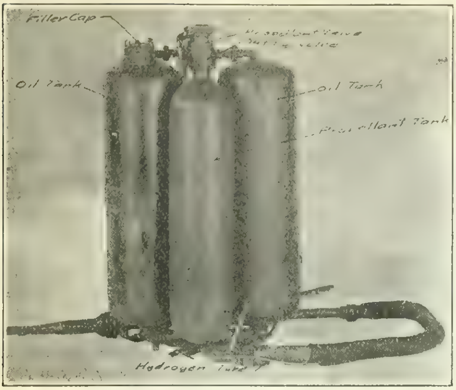


Fig 25—American Portable Type Flame Projector

as the pressure increases up to a definite point, beyond which the stream of liquid is broken up into drops and the length of projection is decreased. For a five-sixteenths-in. nozzle an average working pressure with a moderately heavy liquid is around 250 lbs. per sq. in. and the projection obtained may be over 100 ft.

Both portable and large stationary machines have been employed.

The portable type projectors, carried on the backs of the operators by means of suitable straps and pads, contain from 2 to 5 gal. of liquid, have a projection of from 60 to 125 ft., and may be emptied of liquid by continuous discharge in less than 20 sec. They are used by attacking parties and are usually operated so as to throw a number of shots or jets of liquid instead of a continuous stream. This method of operation prolongs the actual period during which they can be used as weapons, which even under the best conditions, is very short.

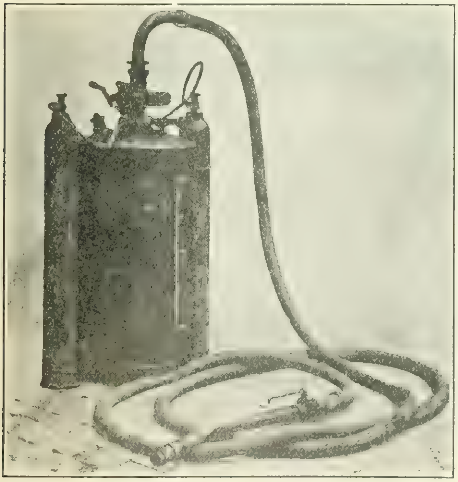


Fig. 26—German Stationary Type Flame Projector Used for Trench Defense

A great many portable projectors differing considerably in many respects have been developed. Some comparative data regarding the most important of them are given in the tabulation which follows:

Data Regarding Portable Flame Projectors

Designation	German Wex	French P3	Italian D. L. F.	British Lawrence	American Boyd No. 3
Weight charged, lbs.	66	53	40	65-70	70
Capacity, gal.	2.5	3.0	1.5	3-3.5	4.75
Propellant	Nitrogen	Air	Air	Carbon Dioxide	Hydrogen
Working pressure, lbs. per sq. in.	288	170	.	240	240
Dia. of nozzle, in.		0.24	.	0.36-0.48	0.31
Range of projection, ft.	80-100	98	83	125	115

The German "Wex" Flammenwerfer shown in Fig. 21 is a late type differing from earlier types chiefly in shape. It has a detachable nozzle from which fact it gets its name ("Wex" from *wechselbarer*—interchangeable). This model has a toroid-shaped oil container, as can be seen, which is made of steel 1.5 mm. thick. The gas container is a steel sphere which fits inside the ring of the oil container and has a volume of about 0.1 cu. ft. Ignition is effected by means of a torch device at the nozzle which is automatically ignited by the pressure of the released liquid and which continues to burn while the liquid is being discharged.

The French P-3 model has separate oil and gas containers and an igniting device attached to the nozzle which is set off by the operator. Other French projectors differ considerably in design and some early ones had no igniting device but depended upon incendiary grenades to ignite the projected oil.

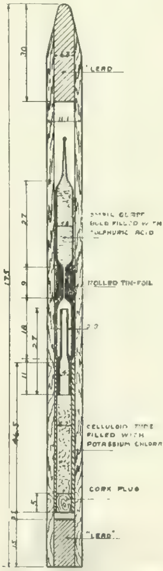

LEAD
SMALL GLASS BULB FILLED WITH SULPHURIC ACID
ROLLED TIN-FOIL
CELLULOID TUBE FILLED WITH POTASSIUM CHLORATE
CORK PLUG
"LEAD"
30
11.1
27
9
18
27
11
44.5
5
15
175
2.3
4

Fig. 27 German Incendiary "Blue Pencil"

The British projector known as the "Hay Flame Gun" (Fig. 22) is unique in that the oil and propellant (carbon dioxide) are contained in the same reservoir. Ignition is effected by a device at the nozzle consisting of a slow burning mixture inserted in a metal holder. This mixture is ignited by an electric detonator, the battery case which furnishes the current being clipped on to any convenient part of the apparatus. This form of ignition is said to be excellent. The machine, although possessing some undesirable features, gives very good results.

The British Lawrence projector (Fig. 23) carries a separate carbon dioxide container inside the oil container, and has practically the same electrically ignited ignition device as the Hay projector. The type and range of projection is shown in Fig. 24. This projector has more good and fewer bad features than any other yet produced.

The American projector, as finally developed, possesses some differences of design from any other models. It has double oil containers for convenience in carrying and a separate propellant cylinder as shown in Fig. 25. Hydrogen is used as the propellant gas and is also used for producing a pilot light for ignition of the liquid at the nozzle.

The large stationary type of projectors designed primarily for trench defense carried considerably more liquid than the portable type and were capable of a much longer projection. This increased projection range is obtained by using a nozzle with larger orifice and operating under a higher pressure. In some models a number of liquid containers are connected to a manifold with the propellant gas cylinders connected to each container. By this arrangement the apparatus is made more mobile because the units are not so heavy.

A large "Flammenwerfer" used by the Germans for trench defense shown in Fig. 26 contained about 45 gal. of liquid. The propellant gas was nitrogen held in the two small cylinders, and the igniting device was similar to that used on the portable type projectors.

The French L-1 projectors consisted of three liquid containers connected to a manifold, three compressed air cylinders, and the necessary valves and projecting nozzle. The total volume of liquid was about 33 gal., the duration of projection 15 sec., and the maximum range of projection 180 ft. The utility of these machines was considered very limited.

The large machines designed by the British for use in emplacements, tunnels, or trenches had a maximum range of projection of 100 yds. Eighty gallons of liquid held in four tanks were projected by means of compressed "deoxygenated air." The ignition device was similar to that used on the portable projectors previously described.

The development of large projectors was not pushed by us because the general usefulness of the machines was questionable.

MISCELLANEOUS DEVICES

Besides the devices such as have been described, which were more or less generally used, a number of special devices were designed for particular uses.

Among these was a very ingenious device used by German spies for causing fires in the cargo of ships. It was called an "incendiary blue pencil" because of its similarity in appearance to an ordinary blue marking pencil. The construction is shown in Fig. 27. In operation the spy nicks the "pencil" with a knife so as to break the point of the glass bulb filled with concentrated sulfuric acid and then inserts it vertically into the flammable material—cotton, sugar, etc. The sulfuric acid begins to trickle down into the reservoir and in time is siphoned over into the potassium chlorate with a resulting incendiary action. A large number of mysterious fires in vessels at sea were traced to these "pencils."

Incendiary cans or boxes were used as a means of defense in dissipating gases in dug-outs and deflecting gas waves. The heat generated by the devices produced air currents which effectively caused the desired results.

Special devices were attached to the gasoline tanks of airplanes, by means of which quick destruction could be effected in case the machines were forced down in enemy territory.

Then there were well worked out schemes for rendering trenches absolutely impregnable by forcing oil and gas through underground pipes to special outlets concealed in front, causing its ignition there when the occasion demanded, and so "producing a regular inferno through which no one could pass!"

Some New Features in Limekiln Construction[1,2]

By **Richard K. Meade**

11-13 E. FAYETTE ST., BALTIMORE, MARYLAND

It is not the purpose of the present paper to present any very logical treatment of the subject of lime burning, but rather to touch on some points of limekiln design which are an improvement over common practice, and it is assumed that the reader is familiar with the general proposition of lime burning in both shaft and rotary kilns.

As a preliminary to the discussion of various improvements to be desired in a limekiln, it may be well to give a short summary of what takes place in the burning of lime We have in limestone calcium carbonate and magnesium carbonate, mixed with certain other chemical compounds as impurities, such as silica, iron oxide, alumina, etc. When limestone is burned, the carbon dioxide passes off, and lime and magnesia remain to form commercial lime.

To decompose calcium carbonate into lime and carbon dioxide, there will be required 1451 B. t. u. per lb. of lime formed. To decompose magnesium carbonate into magnesia and carbon dioxide, there will be required 1318 B. t. u. per lb. of magnesia. Hence, to burn dolomitic lime containing 54 per cent lime and 46 per cent magnesia, there will be required 1380 B. t. u. This explains why a magnesian lime can be burned more easily than a high calcium lime.

In designing a limekiln our object is to build a furnace in which the latent heat of the fuel is put to work to decompose the limestone. This is usually done by burning the fuel and passing the products of combustion through a body of the stone.

In the case of the flame kiln, the transfer of heat from the gases to the stone takes place in the shaft of the kiln. It is not practical to transfer all of the heat from the gases to the limestone, and some of it is always carried out by the gases. Manifestly, as the transfer of heat goes on the gases are cooled; consequently the temperature of the gases when they leave the kiln is an indication of the thoroughness with which this transfer takes place. Usually the gases pass through the arches at from 2000° to 2500° F. and leave the top of the kiln at from 400° to 700° F.

As the heat is transferred to the stone, the temperature of the latter increases gradually until a temperature of 1650° is reached, when no further increase of temperature occurs until the limestone has been completely converted to lime, when the temperature again rises.

SOURCES OF HEAT LOSS

INCOMPLETE COMBUSTION OF FUEL—In order to bring about this transfer of heat most economically, the coal must, of course, first be completely burned. Two common losses which occur are from the unburned coal carried out of the furnace in the ashes and from the carbon only half burned, to form carbon monoxide instead of carbon dioxide.[1]

HEAT CARRIED OFF BY GASES—It is well known that the rate of heat transfer is proportional to the difference between the gases and the material to be heated, other conditions remaining constant. Hence the gases entering the shaft should be at as high a temperature as is possible, consistently with the production of lime of proper quality. The greatest factor in determining the temperature of the products of combustion is the amount of air used for combustion. Thus, if we burn 1 lb. of coal with just the quantity of air necessary for combustion, the gases produced will weigh about 11 lbs. If we use twice as much air as is necessary, the products will weigh 21 lbs., etc. Now, manifestly, if we transfer the heat of 1 lb. of coal to 11 lbs. of gas the temperature of the latter will be much higher than if we transfer this quantity of heat to 21 lbs. of gas.

There is another objection to excess air. Some heat is always carried away by the gases leaving the kiln. This heat is proportional to the quantity and temperature of the gases. Eleven pounds of gas leaving the kiln at 400° will carry off only about one-half of the heat which would be carried off by 21 lbs. Similarly, 11 lbs. of gas leaving at 400° F. will carry off only about one-half the heat which it would at 730° F.

To promote kiln efficiency, therefore, we must cut down to a minimum the excess air used for combustion. Some excess is found necessary in practice, but holes in the fire bed, and the entrance of air during stoking, etc., are to be avoided.

---

[1] Read at the 3rd Annual Convention of the National Lime Association, Hotel Commodore, New York, N. Y., June 17, 1921.

[2] Received June 29, 1921.

[1] One pound of carbon burned to carbon dioxide will produce 14,580 B. t. u., one pound burned to carbon monoxide only 3173 B. t. u.

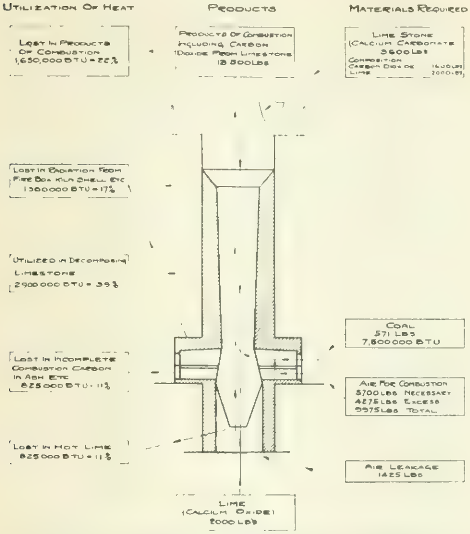

Utilization Of Heat
Products
Materials Required
Lost In Products Of Combustion 1,650,000 BTU = 22%
Products Of Combustion Including Carbon Dioxide From Limestone 13 500 Lbs
Lime Stone (Calcium Carbonate 3600 Lbs
Composition
Carbon Dioxide 1600 Lbs
Lime 2000 Lbs
Lost In Radiation From Fire Box Kiln Shell Etc 1300000 BTU = 17%
Utilized in Decomposing Limestone 2900000 BTU = 39%
Coal 571 Lbs 7,600000 BTU
Lost In Incomplete Combustion Carbon In Ash Etc 825000 BTU = 11%
Air For Combustion
5700 Lbs Necessary
4275 Lbs Excess
9975 Lbs Total
Lost In Hot Lime 825000 BTU = 11%
Air Leakage 1425 Lbs
Lime (Calcium Oxide) 2000 Lbs

Fig. 1—Graphic Illustration of the Reactions in Lime Burning

radiation—Another source of loss of heat is that lost by radiation from the kiln shell.

heat carried off by hot lime—The lime itself carries off a certain quantity of heat, in the ordinary flame kiln. This quantity amounts to 0.22 B. t. u. per lb. of lime per degree of temperature, or about 450 B. t. u. per lb. of lime.

One pound of good coal will liberate approximately 13,000 to 14,000 B. t. u. If we could transfer all of this heat in the coal directly and without loss to the limestone, one pound of coal would burn approximately 8.95 to 9.65 lbs. of lime. Unfortunately, however, we cannot do this and there are appreciable losses, as explained above.

The actual results obtained vary considerably at different plants, but the following may be said to represent good practice in lime burning, or about 3.5 lbs. of lime per pound of coal.

	Per cent
Heat carried off by products of combustion	22
Heat carried off by lime	11
Heat lost by radiation	17
Heat lost by incomplete combustion	11
Total heat lost	61
Heat utilized	39
Total heat supplied	100

In Fig. 1 is given diagrammatically the distribution of heat in lime burning.

To effect economies in lime burning we must eliminate these sources of loss.

The Flame Kiln

Let us take up first the flame kiln and the question of the general design of the shaft. The object here is to transfer the heat from the gases to the stone. In order to do this, we must present to the gases as much surface of stone as possible and bring the gases in contact with this surface as uniformly as possible.

size of stone—Unquestionably, in theory, the best results would be obtained by having the stone in small pieces, because this would present a greater surface of stone to the gases. In practice, however, the small stone presents too great a resistance to the flow of gases, and hence it is probably not possible to improve present practice greatly in the matter of stone sizes. However, it should be remembered that by the use of induced draft (fans) we can overcome to some extent the resistance offered by small stone to the flow of gas. We should also bear in mind that a stone of uniform size, even if small, will offer less obstruction to the flow of gases than will a mixture of large pieces and spalls.

the lines of the kiln—The diameter of the kiln is controlled very largely by the question of distance to which the hot gases from the fire box will penetrate into the kiln, and this depends to a considerable extent on the fuel and draft used. Our own preference has been for a kiln with an oval cross section at and above the fire box, with the lesser diameter along the center line of the fire boxes. Two sides of the kiln are straight down to the cooling cone, while the other two sides are drawn in slightly, as shown in Fig. 1. If drawn in too much—and with some stone if drawn in at all—the charge will stick and hang up in the kiln.

All are, of course, familiar with the fact that if a flat substance

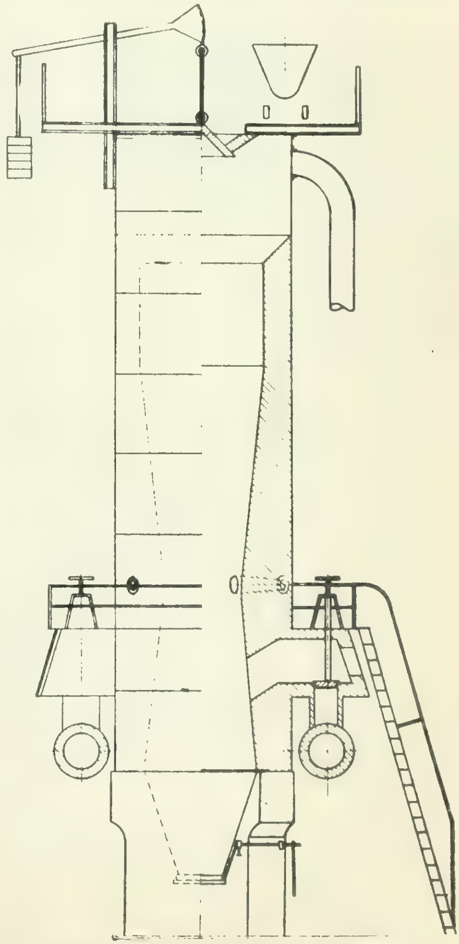


Fig 2—Vertical Lime Kiln Arranged for Producer Gas

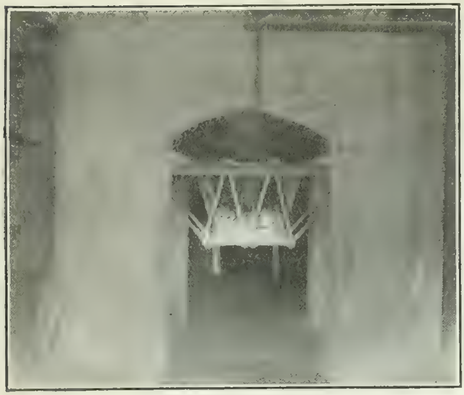


Fig. 3—Quick Acting Drawing Shears and Concrete Pedestal

is brought in contact with the top of a flame, the latter will flatten out. When the gases from the fire box strike the stone the same thing happens and consequently they show a tendency to hug the sides of the kiln, hence the oval cross section.

The writer has generally preferred to flare the kiln out after leaving the burning zone, with the idea not only that there would be less chance for the charge to choke and arch, but also that as the lime spread into the enlarged area there would be a tendency for the charge to roll over and separate, and thus expose fresh surface to the flame. If drawn out through a cylinder of the same cross section it would probably merely sink down in a body

Where we use a gas as a fuel we employ practically the same construction of kiln; that is, we draw the lining in above the gas ports and open it out again below these for the reason explained above. (See Fig. 2.)

HEIGHT OF SHAFT—The height of the shaft above the fire boxes is important. It is pretty generally the practice to follow standard lines in the matter of the height. At the same time it is probable that a careful study of conditions would show that in the case of some stone very much higher kilns could be used with advantage than in the case of others. There is no question but that, within reason, the higher the kiln the better the economy which can be obtained, because a longer time is given the stone to absorb the heat from the gases. The height, however, is limited by the draft produced. Where natural draft is employed there is a limit to the height which is allowable, and 30 to 35 ft. above the fire box is generally considered ample. It is quite probable, however, that by the use of induced draft higher shafts could be employed.

CHARGING—The charging arrangement shown on the top of the kiln illustrated in Fig. 2 will give satisfaction for closed-top kilns used with induced draft. It is similar to those used on the smaller blast furnaces. It is quick acting and closes the opening tightly, preventing any cutting down of the draft due to air leakage here. If each kiln is provided with its own individual fan much better operation will be secured. This arrangement is particularly desirable where the fans can be directly connected to electric motors.

STONE BIN—Practically all of the newer kilns employ a stone bin on top of the kiln. This is really part of the shaft but, as the temperature at this point is low, the bin is usually left unlined. There is no question about the advantages of the stone bin, and, for practical purposes, the larger it is the better. The idea, of course, is always to have in the shaft of the kiln a body of stone sufficient to absorb the heat properly. If the stone bin is made of the general design of the shaft, the gases probably pass up through the bin with some degree of uniformity, and it serves not only to hold the stone for the time when the kiln is not charged, but also as part of the shaft.

COOLING CONE—Most of the better types of kiln are provided with a cooling cone. This is made of steel plate and is so placed that the lime is cooled almost entirely by radiation. The ideal arrangement for cooling the lime would unquestionably be one in which the air necessary for combustion passed up through the lime and cooled the latter, and thus recovered the heat carried off by the lime. In the case of coal-fired kilns, no practical method has been worked out by which this result can be achieved. In the case of gas-fired kilns, however, the air for the combustion is allowed to enter at the bottom of the cone, passing up through the lime and abstracting the heat from the latter.

It would probably be better to allow the shaft to project for 4 or 5 ft. below the fire boxes before the steel cone is placed on the latter. This would leave a considerable body of hot lime below the burning zone. No heat can be transferred from this hot lime to that being burned because radiation takes place only from a hotter body to a colder one, but there is always considerable air which enters the kiln where the lime is drawn and the hot body of lime below the arches would serve to heat this and prevent its cooling off the limestone in the burning zone. There is a mechanical objection to the use of such a form of cooler, however, in that it would necessitate raising the fire boxes about 6 or 7 ft. higher from the floor.

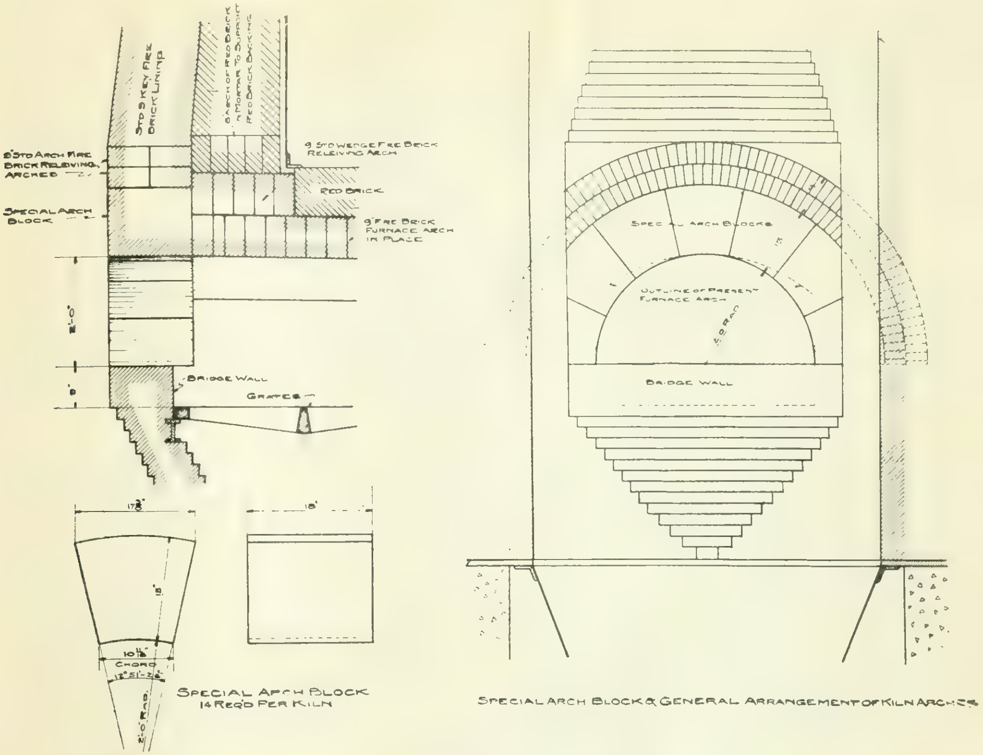
QUICK-ACTING DRAW—Attention has been called to the desirability of reducing to a minimum the excess air entering the kiln.

Unquestionably the largest thermal loss is in the excess air which enters the kiln at the time of discharging the lime and during the stoking of the fire. The former may be cut down to a minimum by the use of a very quickly acting draw on the cooling cone.

Fig. 4—Forms for Pedestals

For use on our kilns we have designed a very quickly acting draw which is shown in Fig. 3. The doors may be adjusted by means of lock nuts to an accurate fit with the bottom of the cone, and, as they are swung from beams resting in the concrete pedestal and not from the cone itself, they are not affected by the warping of the latter. The doors are opened and closed by a single push and pull on the operating levers. These latter are located outside of the kiln and permit the operator to stand away from the dust and heat when the lime is being drawn.

Allowing a hot body of lime to remain at all times between the


3" Std 9 Key Fire Brick Lining
9" Arch of Red Brick in Mortar to Support Red Brick Backing
9 Std Wedge Fire Brick Relieving Arch
8" Std Arch Fire Brick Relieving Arches
Red Brick
Special Arch Block
9" Fire Brick Furnace Arch in Place
4'-0"
1'-6"
Bridge Wall
Grates
17 3/8"
18"
15"
10 1/4"
Chord
17°51'-24"
Spec Arch Blocks
Outline of Present Furnace Arch
Bridge Wall

Special Arch Block
14 Req'd Per Kiln

Special Arch Block & General Arrangement of Kiln Arches

Fig. 5

cooling cone and the burning zone will also reduce the loss of heat due to the drawing of the lime, as we have said.

HAND STOKERS—We have recently tried hand stokers in place of the ordinary hand firing in order to cut down excess air used to burn the coal. The quantity of coal consumed in a single furnace of a limekiln is not large enough to warrant the installation of mechanical stokers such as are used on boilers and large furnaces. There are a number of hand stokers which have been successfully used for heating small metallurgical furnaces, and one of the most successful of these has been adapted to our type of limekiln. The result has been to increase greatly the capacity of the kiln, cut in half the labor necessary for stoking, and decrease materially the fuel consumption. We also find that with the kilns on which we have tried this stoker there is practically no core obtained, whereas on the same kilns without the stoker the core will probably run to about as much as 5 per cent of the lime. In view of the increased kiln output obtained by the use of stokers, this is one of the cheapest ways of increasing the capacity of a flame kiln lime plant.

PREVENTION OF HEAT LOSS BY RADIATION—Next to the excess air, the largest item of waste in lime burning is unquestionably due to radiation from the walls of the fire box and the kiln shell. It is, therefore, better practice to prevent this as much as possible. A new material which is both cheap and efficient is sil-o-cel. This can be obtained in blocks, but a more satisfactory form for the use in limekilns is the powder. It is quite the general practice to fill in between the brick and the shell with a thin layer of sand. An appreciable saving of fuel can be effected by the use of sil-o-cel in place of this sand backing.

STRUCTURE OF KILN—Referring to the structural features of the kiln, the most popular material for the shell is steel. There are some points, however, in favor of reinforced concrete. It is generally known that steel will radiate heat more rapidly than concrete. Some heat is therefore saved by the use of a concrete shell. The concrete shell is also more permanent, in that it does not require continual painting and is not subject to corrosion from the acids generated from the sulfur in the coal.

In some types of kiln the steel is run below the firing floor. This has seemed rather expensive construction, however, and we have built our kilns on concrete pedestals. Wooden forms are used and are moved from one kiln to the next during construction (Fig. 4).

A weak point in the flame kiln has always been the arches. The writer has tried out several different kinds of brick, but his preference is now for specially made blocks of large dimensions and of exact key to fit the radius of the opening between the kiln and the firebox. We use a block approximately 17 x 11 x 15 x 18 in. and use one row of these. Fig. 5 shows this block, which is much stronger than the standard 9 in. brick. They have a much larger key and wedge in more firmly. Owing to their weight, these blocks are not easily pushed out of place by a bar when poking down a hang-up. As they are specially made, the manufacturer will usually see that they are better burned and annealed and made of better clay mixtures than his standard brick.

The cooling cone has always been a weak spot in limekiln construction, and at some plants the advantage of obtaining cool lime has not proved sufficient to compensate for the frequency with which the cone has to be renewed. We have found that the life of the cone can be considerably increased by proper ventilation at the top, so that a current of air can pass around the cone at this point. As generally placed, the top of the cone is in a confined space and the air at this point is practically stagnant. By placing a few vents so that the air can pass up between the cone and the side of the kiln, a current of air can be made to pass around the cone at this point and reduce its temperature materially and increase its life. If desired, this air may be conducted into the firebox below the grate, but it is doubtful whether any appreciable saving in fuel would be effected thereby.

On the last kilns which we have built, we have employed a water jacket around the upper part of the cone, the idea being not only to cool the lime but at the same time to protect the cone. We have made no effort to water-jacket the whole cone, but only a space of about a foot, as near the top of the cone as the jacket can be placed.

We have always made the platforms and walkways on top of our kilns of steel. For the floor plates we usually use perforated steel plates or a better and more rigid material—Irving's subway grating.

THE ROTARY KILN

Turning our attention next to the rotary kiln, the losses here are practically the same as in the flame kiln. The losses due to radiation and to heat carried off by the products of combustion are greater than with shaft kilns, while the losses due to incomplete combustion and heat carried off by the lime are less. A complete general discussion of the rotary kiln lime plan and a comparison with flame and gas fired kilns will be found in *Rock Products* of December 4, 1920.

PULVERIZED COAL—The principles of heat transference are the same in rotary kilns as in shaft kilns. It is desirable to have a high initial flame temperature and to cut down to a minimum the excess air used in burning. Pulverized coal is much easier to regulate than producer gas and gives a higher flame temperature. Consequently it is to be preferred to producer gas when good coal low in ash can be secured. With pulverized coal, we can cut down the excess air used in burning to almost the exact amount required by theory, and we can also burn our fuel completely.

Pulverized coal is unquestionably a more efficient fuel for heating the rotary kiln, than producer gas, and where complaints as to the fuel economy of the rotary kiln have come to our attention, we have usually found that the gas producer was at fault and that the heating value of the gas supplied the kiln was low. It must be remembered that in gasifying coal some of its heating value is lost, so that the gas which is made from a ton of coal will not have the same number of heat units as this amount of coal itself. These losses in even the best gas producers are at least 10 per cent and often will run as high as 25 per cent, with perhaps 15 to 20 per cent as an average loss for mechanically stirred producers. In pulverizing coal, none of its thermal value is lost, so that we get the full heating value of the coal. In addition to this, pulverized coal can be burned completely, and the quantity of excess air necessary to do this is probably smaller than with any other fuel.

We must also remember that with pulverized coal we are feeding into the kiln a uniform stream of fuel of the same heating value at all times, whereas with producer gas the quality of fuel fluctuates with the condition of the producer.

By the use of pulverized coal, we introduce into the products of combustion in the kiln itself practically all of the heat units of the coal. The combustion is almost perfect, and there is no loss of heat due to carbon in the ash or to radiation from the producer walls and gas piping.

PRODUCER GAS—The only producers which will give satisfaction and good fuel economy with either vertical or rotary limekilns are the automatically stoked, and preferably automatically fed, producers, as they can be made to furnish a constant supply of gas of uniform quality.

Where producers are used in order to improve the quality of the lime they should be set close to the kiln in order to reduce to a minimum the loss by radiation from the gas mains.

FACTORS INFLUENCING ECONOMY—In a general way, it may be said that better results will be obtained by a large body of material moving slowly through the kiln than from a small body of stone moving rapidly. This means the kiln must not be pitched at too great an inclination.

If the diameter of the kiln is too large compared with the length, the fuel requirements will be high. Other things being equal, the longer the kiln the better fuel economy.

The size of stone burned influences the economy to some extent. As a general rule, better results can be obtained by screening out the dust from the coarse rock before burning. This dust also contains a large part of the dirt which finds its way into the quarry, so that its removal is of advantage in increasing the purity of the lime. In localities where water is abundant, there would be no objection to washing the limestone to free it from dirt, as the wet stone would not affect materially the operation of the kiln.

For best production and economy, the stone should pass a screen with round perforations 2.5 in. in diameter, and should be retained on a screen with round perforations 0.25 in. in diameter.

WASTE GASES—In spite of the best efforts to transfer the heat from the gases to the stone, the exit gases will always contain considerable heat. The weight of exit gas will be smaller than with flame kilns because we can control the combustion better, but the temperature of the gases will be much higher because the conditions for heat transference are not so favorable.

The waste gases usually leave the kiln at about 1300° F., and hence contain a considerable part of the heat liberated by the burning fuel. This heat can be successfully utilized in boilers, as has been done in the cement industry, where an efficiency of 70 per cent has been obtained. The weight of gases usually amounts to between 6500 and 7500 lbs. per ton of lime produced. The heat in these gases will, therefore, be approximately 2,275,000 B. t. u. or the equivalent of 165 lbs. of coal. Of this waste heat, 70 per cent has been successfully utilized by waste-heat boilers or about 1,500,000 B. t. u. per ton of lime produced. This is equivalent to 1550 lbs. of steam at a temperature of 212° F., or 45 boiler horse power hrs. A kiln burning 4 tons of lime per hr., therefore, would be good for about 180 h. p. Most lime plants are operated in connection with crushing plants, or mills for grinding lime, pulverizing limestone, or hydrating lime, so that this power can generally be utilized. The kiln and accessories will not require more than one-third of this, leaving about 120 h. p for outside uses.

Where power is required for other purposes in the works, therefore, the installation of waste heat boilers and a crediting of the coal which would otherwise be required to generate this power to the kiln, will greatly increase the efficiency of the rotary kiln.

ROTARY COOLER—By the use of a rotary cooler, properly set, the heat carried out of the kiln by the lime can be recovered. The cooler should be so placed that the hot air will pass into the kiln. Thus the cooler will serve to preheat the air for combustion. The cooler should be provided with Z-bars or angle-irons, which serve as lifters, carrying the material up and dropping it through the current of air passing through and so adding to the efficiency of the apparatus (and incidentally also to the dust loss). The cooler may also be divided longitudinally into four compartments which serves the same purpose. If the dust proves too great the Z-bars may then be removed from the latter form of cooler without too great loss of efficiency.

As has been said, the radiation loss is quite large from a rotary kiln, but this can be reduced materially by the employment of a lining of sil-o-cel blocks between the regular fire brick lining and the steel shell.

CHEMICAL CONTROL IN FUEL ECONOMY—The completeness of combustion can always be determined by an analysis of the waste gases of the kiln whether it be gas- or grate-fired, and the temperature of these gases will show how well the heat has been transferred to the stone. Pyrometers in the walls of the kiln, properly protected, will show the conditions and rate of burning also. Neither the pyrometer nor the gas analyzer requires trained chemists. Any intelligent workman can be broken in to use both, and even to interpret the results in terms of kiln efficiency. The latter, so far as the exit gases are concerned, is summed up in three phrases—low carbon monoxide, high carbon dioxide, and low temperature.

Standardization and Research[1]

By S. W. Stratton

Chief, U. S. Bureau of Standards, Washington, D. C.

Standardization and research go hand in hand. The term "standardization" has come to mean a great deal more than it did formerly. We used to think of standardization in connection with measurements simply; then we passed on to measurements in all the various branches, and then to measurements of specifications.

Standardization of Quality

A specification is nothing more than a standard of quality, and we find that such standards are absolutely necessary if we are going to use materials intelligently. One of the greatest factors in this standardization is arriving at definitions, which we understand to mean agreeing upon definitions of materials. All of this enters into the standardization of quality, and in many ways places industry upon an entirely different basis in its dealings with the public. The public needs education in the use of all of these materials, and it is the business of the Bureau to bring together the public and the manufacturer on a common ground and to teach the public to understand materials. We do everything we can for the manufacturer and the public in improvement of quality.

Simplification of Standards

There is another kind of standardization which has come very much to the fore recently, which we have termed simplification. Mr. Hoover, in his work on standardization, is very much interested in this part of it. It means confinement to the fewest number possible of sizes and varieties of manufactured articles. You may have twenty sizes and varieties, whereas three or four would answer every purpose. In some of these materials we need varieties and sizes, but we want that variety to be as small as consistent with public needs, and we want each variety to be carefully defined so you can speak of it in terms which both the public and the manufacturer can understand. This term "simplification" is a very important factor in our economical program. The Secretary is very much interested in this feature of standardization, and Congress has recently given us some money to carry out this work. We believe we are going to be of much greater assistance to you in the future than we have been in the past.

Dangers in Standardization

Standardization is a very dangerous thing if it is not carefully carried out. In the first place, several parties are concerned in it—the man who makes, the man who uses, and the man who has actually set up the definitions. A definition or specification amounts to nothing if we haven't the proper test and if we haven't proper methods. All of those things go into the question of standardization. Now, the laboratory has no more right to set up and make these standards alone than has the manufacturer or the user. We have had a lot of experience in the government service; we have set up standards for government departments and bureaus, and we find that the government departments furnish excellent examples of users—you can find users of almost every article that is utilized—and what is more, we can coöperate with those users. It is not an infrequent thing for us to ask an officer of the Army or the Navy or of some other department to follow up the use of the material and to keep as close to us as he can. That is a very important thing in standardization—the following up of materials in actual use.

There is another danger in standardization, that it may become too fixed. If it is a question of standards of measurement, we want them to be fixed. We try to fix standards that we can refer to from time to time and feel that they are constant. Now, as to quality, it is exactly the reverse: We want the standard to be improved as the art advances, and there again it is only by close coöperation of those concerned that we can bring about a proper standardization. The Bureau of Standards method, as you know, has always been to bring about a sort of voluntary standardization. That is also the Secretary's idea.

At a recent meeting of users of paper, together with a committee of paper manufacturers who had come down to coöperate with the Bureau in setting up the standards of paper, we found ourselves face to face with standards which had been prepared without coöperation with the manufacturer. It was perfectly evident that the users in this particular case had made these specifications from their own practice. They had neglected important principles, as well as certain features of definitions of paper. At the request of these manufacturers the Bureau will undertake to set up standards; that is, with the aid of these people and with the aid of the users, we will set up standards of paper that the public can use and keep them up to date from year to year.

Need of Laboratory Control in Standardization

In this question of standardization there is always one where the laboratory can be of important use. When we set about bringing together the manufacturer and the user, we find many traditions and many customs. Scarcely a case of this kind comes up where there is not a great difference of opinion as to some point. Now, the laboratory steps in and tries to settle it by actual experiment. The laboratory, with the manufacturer's knowledge and use of the material, can decide these questions, but they cannot be decided by a mere sentiment or tradition. Controlled in this way, standardization will progress as it should.

Research in Standardization

Just a word in regard to research. It is almost unnecessary to speak to an audience of this kind of the value of research. There are certain kinds of research that can best be carried on by you at your work, where the benefit that accrues to research should apply to the plant itself. Then, again, there are researches in which you as an organization can join hands and work out once for all. That is the economical way to do it.

Some of these things which are needed in standardization are fitted for government research; but there is another class in which

---

[1] Read at the 3rd Annual Convention of the National Lime Association, Hotel Commodore, New York, N. Y., June 15, 1921.

I am especially interested, and which the Government is peculiarly fitted to carry out, namely, those researches which call for the highest kind of scientific work for the benefit of an industry as a whole, and which partake very largely of the nature of fundamental scientific research. You can never tell when this fundamental scientific research, or its results, is going to be used. It is fortunate indeed that we can predict beforehand what these researches are going to be. There are certain things, for instance, that you want to know about lime. We will go at the fundamental question and try to find out just what lime is, how it behaves, what the laws governing it are. Then we are in a position to handle these problems and a great many more. We see many examples of this thing. Just a short time ago we were called upon to standardize color. We haven't many standards of color. The cottonseed oil people were the first to take it up. We have established these standards of color, but, of course, in applying it to such a thing as cottonseed oil we must have a sample of the oil we can compare, that is, a working standard throughout the year and throughout the season. We found that the oil specimen which was to be used as a standard for the year would change rapidly, and therefore we began to experiment upon the nature of this oil. We found out that if we took the air from it—it absorbs air in rather large quantities—its color did not change. That is what we were striving for. But think of the by-product that came out here. We also found that when we took this air from the oil it did not become rancid. This was worth a great deal to that industry. To-day factories have been built, utilizing this principle to prevent the various oils from becoming rancid. It was a discovery which was worth as much to that industry as the whole cost of this Bureau to the Government.

We need to know more of the nature of the materials. At the Bureau we have various sections—on lime, clay products, metals, lubricating oil, paper, rubber, and all such materials. We have a 30-inch rolling mill; we have a textile mill; we have all the facilities necessary for giving to these workers a variety of materials which they never could get before. As far as the paper mill is concerned, we now can have any kind of paper we wish, we can go to work and experiment with that paper. Paper manufacturers are bringing their problems there, and thus research is carried along those lines which the Government is better fitted to accomplish.

I am sure that the Department of Commerce as a whole can be of great assistance outside of the Bureau of Standards, in the Bureau of the Census, which gathers statistics, and the thing for you to do is to ask for the statistics you want. The Bureau of Foreign and Domestic Commerce can do a great deal for the lime industry. We must get over this idea that the departments of the Government are policemen to tell you what to do. It is the reverse: you are going to tell us what you want us to do. It is for that reason that we are taking this new method of procedure in the Department of Commerce and trying to make it useful and a real help, as it should be.

Industrial Application of Certain Research Investigations

Before closing there are one or two rather interesting illustrations about the value of research in standardization I would like to mention. They have nothing to do with lime. However, I do know that just before I came here we sent letters to men, many of them who are members of this Association, asking them about the standardization of lime. Out of that will grow a definition and specification about which those who use the lime will know, and which you know you can make. Many important investigations are going on in this lime section of the Bureau and you will get returns worth many times what it cost.

PHOTOGRAPHIC PLATES—Before the war one of our spectroscopists was asked to photograph the spectrum to determine the wave lengths of light needed by an astronomer for his use. The region assigned to us was the red end of the spectrum, the most difficult to photograph. I am taking this illustration because an astronomer is the type of man working on abstract science. In order to photograph this end of the spectrum our expert experimented with dyes, with the various plates, and with certain other work that had been done before, which gave the clue, and out of which grew a method of sensitizing the plate to make it sensitive to red light. We could thus photograph much further down in the spectrum than we could before. Now, these red waves have the power of penetrating a fog much more readily than short waves. During the war it was necessary, as you know, to depend almost wholly upon the photographs made by airplanes in getting maps of the country, and by the use of these same planes we got photographs of things that could not be seen without them. Now, what is next? This is just as important in all kinds of commercial photography and in moving pictures, and it will only be a short time before these plates will be the ordinary thing and the old plates will be an exception. That is a case where, in starting its investigation, the Bureau had solely for its object abstract data for an astronomer, which has turned out to be very important commercially.

MANUFACTURE OF BLOCK GAGES—One of our experts is working on methods of measuring by means of light waves. We use light waves to measure small quantities—light waves about one-fifty-thousandth of an inch long—but for some purposes it is the only kind of yard stick that we can use. We can establish it anywhere we like with certain apparatus. It will be only a short time until all our standards of light are fixed by light waves. By this method of light waves we are making what is known among mechanics as block gages—ordinary blocks of metal of a definite length; that is, the two faces must be parallel to each other, they must be an exact distance apart, and the faces must be plane. By parallel, we mean within a very small amount, and by plane, we mean within a millionth of an inch, and the length must be correct within two- or three-millionths of an inch. This means the most accurate measurements that have ever been made. These gages were formerly imported. When the war broke out we were absolutely cut off from them. Now by these light waves we make the gages and test them.

LIGHTING EFFICIENCY—Our program of economy is going to be based upon our improvements. We told the appropriation committee that it is wise to spend money in order to save money. It has been very difficult for them to see that, especially as everybody else looking for money there tells the same story. You know that in the old days of the oil lamps we got a certain efficiency; then came the gas lamps and following that came the incandescent lamps, and now we have the tungsten lamps and the gas-filled lamps, and we have kept pushing the efficiency up and up all the time until we have reached the limit. Now, the efficiency that you can get out of your lamps is a very small proportion of the energy that is put in; there is a tremendous waste. How are you going to improve it? We can't do it by going along the same lines. So the next step which we are trying to accomplish is to find out about the nature of radiation. We have a young man at the Bureau who is working on the structure of the atom. To-day we speak of the atom just as you would of the universe. We speak of the inner range and the outer range, of the parts of an atom, and of atoms being knocked against one another. Here is a young man who is working on this question pertaining to the atom, how constituents of atoms can be knocked from one place to another just as a workman handles bricks and lays them up with mortar. Now, what is the object of all that? When we know the story of matter, when we know how it is built up, and how this radiation comes? It comes from the atom. We can probably take the next step in the improvement of the efficiency of lamps.

The Measurement of Color[1]

By C. E. K. Mees

Eastman Kodak Co., Rochester, New York

The chemical industries are largely concerned with objects having a definite color. The measurement of color must be of considerable interest to the chemist engaged in the dye industry, the paint industry, or the textile industries, while even those who work in such fields as the chemistry of the vegetable oils or similar food products frequently desire an accurate and simple method of measuring the color of the materials which they make.

Methods of Color Measurement

The methods of measuring color fall into two distinct classes, according to whether we wish to measure the sensation of color produced upon the observer, or the stimulus which produces that sensation. While different sensations are always produced by different stimuli, the converse is not true, and quite different stimuli may produce the same sensation. Thus, a sodium flame appears to the observer a bright yellow color, and a dandelion also appears a bright yellow color, its color approximating very closely in appearance that of the sodium flame; but the stimuli are quite distinct when analyzed, the sodium flame giving rise to only a single monochromatic ray of light, while the dandelion reflects almost the entire spectrum, absorbing only the blue.

The Spectroscope

When measuring the stimulus which produces the sensation of color, we must use analytical methods, because of the composite nature of light itself, while when dealing with the sensation itself, synthetic methods of measurement must be employed. The analytical instrument used in studying the stimulus of light is the spectroscope, which depends on the differential effect produced by a prism or a grating upon light waves of different lengths. When a beam of mixed waves of light, such as white light, is passed through a prism, it is refracted differently according to the wave length of its composite parts and is spread out into a colored band termed the *spectrum*.

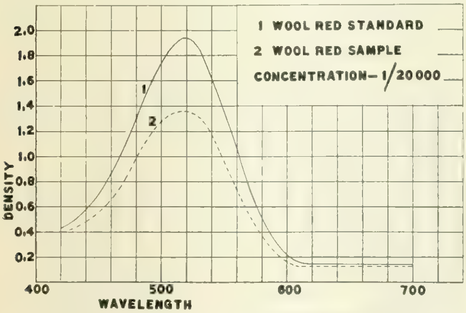


Fig. 1—Spectral Absorption Curve for Red Dye

The Spectrophotometer

The quantitative measurement of color is undertaken by means of an instrument termed the *spectrophotometer*, which is essentially a spectroscope with photometric attachments. In this instrument, any portion of the spectrum can be isolated and divided into two portions having the same color and adjacent to one another. Into one of the beams is introduced the colored object to be measured, which produces an absorption of the spectral region in question. The other beam is then darkened by some photometric means until the two patches, as seen through the eyepiece of the instrument, appear of equal intensity. Since the amount of darkening which has been introduced photometrically is known and is equal to the amount which has been caused by the absorption of the colored object, we can read from the instrument the quantitative value of the absorption at any point of the spectrum. This is repeated throughout the spectrum, step by step, and a curve of absorption against the wave length of the spectrum is obtained; thus, if we have a red dye solution, we shall obtain a curve similar to that shown in Fig. 1. The abscissae of the curve represent wave lengths of light, and the ordinates represent the absorption in units inversely proportional to the thickness of the solution which will produce a transmission of one-tenth of the original intensity. It will be seen that the red dye has a slight absorption in the blue, rising very rapidly to a strong maximum in the green at a wave length of about 520, and falling off again until, at a wave length of 600, it is transmitting almost all the light.

The readings of the spectrophotometer are directly proportional to the concentration of the dye solution, and it can thus be used for measuring the concentration of a dye of unknown strength. All that is required for this analysis is a standard sample of dye which is known to be pure. A solution of known strength is made from this standard, a solution of the sample to be analyzed of the same nominal concentration is prepared, the two solutions are read on the spectrophotometer, and the absorption coefficients obtained on the instrument are compared. The concentrations of the dyes are in the same proportion as their absorption coefficients.

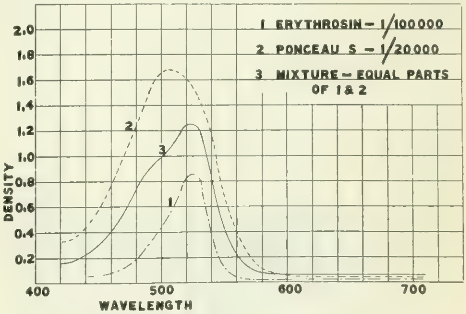


Fig. 2—Spectral Absorption Curve of Erythrosin

The spectrophotometer is suitable not only for the analysis of finished dyes, but also for following reactions involving changes in color. Thus, when fluorescein is iodinated in the preparation of erythrosin, the progress of the reaction can be followed very simply and accurately by taking a spectrophotometric measurement of the product. There is little doubt that the application of the spectrophotometer in the dye works would result in economies in manufacture. In the research laboratory, the spectrophotometer can frequently be applied to the investigation of physicochemical conditions; dyes which are partly in crystalline and partly in colloid solution, for instance, will give different absorption spectra according to their condition. As a qualitative instrument, the shape of the curve is of value in identifying substances. Thus, in Fig. 2 we see the curve of erythrosin as the dotted curve, while the solid curve shows a sample of erythrosin submitted during the war which is clearly not the same substance. As a matter of fact, it is adulterated

---

[1] Presented before the General Meeting at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

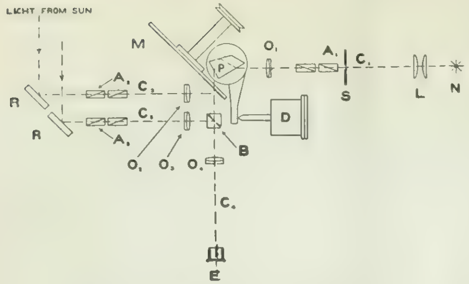


FIG. 3 DIAGRAM OF MONOCHROMATIC ANALYZER

with Ponceau Red, as can be seen by comparing it with the curve of Ponceau Red, shown as the dashed curve.

THE COLORIMETER

The spectrophotometer, however, does not give any direct indication of the color of an object. If we know the spectrophotometric reflection curve of a colored paper, the visibility curve of the eye, and the energy curve of the light falling upon the paper, it is possible to calculate the resulting color, but the calculation is by no means simple, and it is far easier to measure the color directly as the sensation, by means of an instrument known as the *colorimeter*.

The sensation produced upon the eye by an object may be specified as the brightness (dependent upon the intensity of the light) and the color (dependent upon the quality). The color can, in turn, be analyzed into the hue and the saturation, either of the components being capable of change independently. Thus, starting at the red end of the spectrum, we may have a red, an orange, a yellow, a green, a green-blue, a blue, or violet color, these terms giving the approximate hue. Any of them may be diluted with white, so that we may get pale colors of each hue in turn. Moreover, we may get the group of colors which is not included in the spectrum—the purples, violets, and magentas—which are complementary to the green. These may be specified most conveniently by the green hue to which they are complementary.

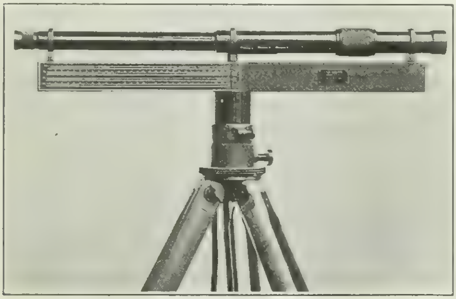


FIG. 4 -EASTMAN COLORIMETER

The easiest method of specifying hue is by means of the wave length in the spectrum which corresponds to the hue in question. Thus, we may specify a red as being of dominant hue wave length 650, corresponding in hue to the color of the red hydrogen line. A yellow might be of dominant hue 580; 570 would be a greenish yellow; 560 would be a yellowish green.

THE MONOCHROMATIC ANALYZER

On this division of color into hue and saturation is based the most satisfactory and convenient colorimeter, the monochromatic analyzer. In this instrument the color to be measured is balanced by means of a mixture of a spectral color and white light. Thus, in order to measure a green tinted paper, we place the paper so that the light reflected from it falls into the colorimeter (Fig. 3). In the photometric field at B, we see one part of the field filled by the green light from the colored paper. The other part of the field can be illuminated by means of a spectrum to which can be added any proportion of white light that is required. We change the wave length of the spectral light by means of the drum until the hue appears approximately right. We next add white light from the beam C_2, reflected from the glass surface M, until an approximate match is obtained, keeping the intensity of the two fields the same. The hue may now require a little correction, and when this is almost exactly right, the admixed white may require another correction. By this method, very rapidly used after a little practice, the color is matched exactly by the other field. The dominant hue is now read off directly from the spectral drum, and the percentage of admixed white light measured photometrically in the instrument. This is the only form of colorimeter which reads the color directly in absolute units, namely, the wave length of the dominant hue and the percentage, but simpler forms of colorimeters may be made in which the color to be measured is compared with a mixture of known color.

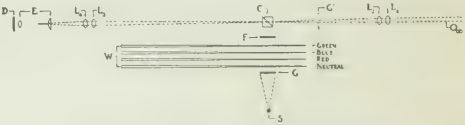


FIG. 5—DIAGRAM OF EASTMAN COLORIMETER

THE TRICHROMATIC ANALYZER

A representative instrument of this kind is the trichromatic analyzer, in which the color is matched by a mixture of three colors transmitted through three separate color filters corresponding to three regions of the spectrum. The proportions of the three colors required to match the color to be measured are read from the instrument, and by recording them, the color can always be reproduced in the instrument.

ANOTHER TYPE OF COLORIMETER

A simple instrument of another type which is very suitable for works use has been designed by Mr. L. A. Jones of our laboratory (Figs. 4 and 5). It has the advantage of not requiring a spectrum or any special mixing device and of being very robust in its construction. It is based on the subtractive principle, depending upon the use of colored wedges, each wedge absorbing one-third of the spectrum, so that the three wedges are yellow, blue-green, and magenta in

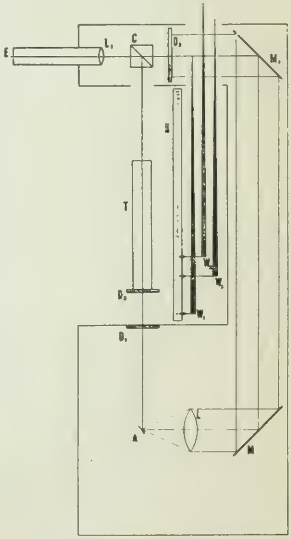


FIG 6—COTTONSEED OIL COLORIMETER

color, the yellow wedge absorbing the blue of the spectrum, so that it may be called *minus blue;* the magenta absorbing the green of the spectrum, so that it may be called *minus green;* and the blue or *minus red* wedge absorbing the red of the spectrum. When these wedges are placed over each other in pairs, they will give any color possible, provided that the intensity is adjusted at the same time by the use of a neutral gray wedge, which is supplied as the fourth wedge of the instrument. The instrument can be made with a number of attachments, according to the purpose for which it is required. Thus, colored solutions, colored glasses, and colored papers can all be measured by suitable attachments. A modified form of the instrument has been designed for use in measuring vegetable oils, notably cottonseed oil. A diagram of the Eastman cottonseed oil colorimeter is shown in Fig. 6.

There is no doubt that colorimeters are just beginning to be used, and that their use will rapidly increase in the industries, and, above all, in the chemical industries. At the same time, the analytical measurement of color by means of the spectrophotometer will increase and will find many applications which are not at present apparent.

SOCIAL INDUSTRIAL RELATIONS

Out-of-Door Education for the Chemist

By H. W. Jordan

Syracuse, N. Y.

August is the peak of out-of-door life. Most of us succeed in getting back for two weeks to woods, lake, or seashore to re-create ourselves in preparation for the strenuous demands of laboratory or works, through fifty more weeks. The change and rest of the yearly country outing is only a part of its possible value. Out-of-door education is beginning to be recognized as a most promising means of making common school education the most adequate preparation for social, industrial, city life.

Among proofs of this tendency is a recent article by W. C. Ryan, Jr., Educational Editor of the *New York Evening Post.* Under the title "Summer Camps Blazing Way in Education," he points to these camps—on mountain side and lake shore—as the prophetic symbol of the newer American education. "The value of the outdoor life in the sunshine, amid forests and lakes, with wholesome companionship, is incalculable. The opportunities afforded tend to bring the boy into closer kinship with nature, develop his manliness, stimulate good fellowship and a spirit of generosity. He cultivates self-reliance, self-respect and regard for others." Out-of-door life prepares the boy for coöperative, industrial life.

"Is it not a pity that ideals like these cannot make themselves felt more in our entire program of education for the benefit of all youth, instead of merely for the 5 and 10 per cent of American children who at most profit by them?"

IN OUR PROFESSION OF CHEMISTRY, WE ARE CALLED UPON DAILY TO EXERCISE OUR SENSES AND OUR REASON, AS WE MUST WHEN LIVING OUT OF DOORS—The character of the precipitate, the shade of the dye, the cellular structure of the coke, the fracture of the pig, the intensity of the reaction, these and all chemical or physical conditions must be sharply, correctly observed, and right conclusions must be drawn. Just as, in camp, we need to forecast whether the wind will raise the water at our end of the lake and damage our boats during the night; need to observe the habits of fish, that we do not waste our time drowning worms instead of dropping them overboard at the exact place and hour when fish are keen for food; need to know the lay of the land, the position of the sun and stars, and the growth habits of trees, to guide us back if lost in the woods.

"The good hand fisherman is the man who can feel correctly what is going on at the fish hook out of sight, and can make his motor nerves react quickly to what he feels there," says President Eliot of Harvard.

There is no better boyhood training for a research chemist than a series of summers spent in the woods with councilors of the John Muir and Enos A. Mills type, who love and understand nature, and who saturate the soul of the boy with science of field and forest.

"I raised my four boys in the country to give them an experience that would make them self-sufficient, introspective, capable of doing things on their own initiative. Nothing emphasizes a boy's personality more than to find himself frequently alone and forced to depend on his own resources," says Professor Dallas L. Sharpe of Boston University.

MAN WAS AN OUT-OF-DOOR ANIMAL UNTIL RECENTLY—Furnaces and steam were curiosities to our grandparents seventy-five years ago, to be seen only in the homes of the wealthy. Open fireplaces with a kitchen stove, and sometimes one or two airtight stoves, were the only heating outfits in the best of homes. Fires were of wood, usually out at night. Indoor conditions were a pretty good imitation of out-of-doors, most of the time.

Within the lifetime of not more than four generations, not farther back than our great-great-grandparents, we have shifted from an agricultural, out-of-door people to an industrial, indoor people. This is a chief, fundamental cause of many most pressing problems of government, and of industrial and social life, and of education. We have got under cover so quickly that we have not yet learned how to act. We cannot drop habits of a million years' growth in a century and a half, without sustaining some severe shocks.

In the shift we have acquired a lot of new, high-priced diseases, most of which spring up inside us because we do not get enough exercise. If we work sixteen hours a day on a farm, in a lumber camp, or catching cod and mackerel from a dory, we have no trouble digesting salt pork, fried potatoes, baked beans, Boston brown bread, cream of tartar biscuits, and pie. We need no pepsin tablets or Nujol. We do not have to have our teeth pulled to relieve the distress at our stomachs. And the arches of our feet retain that same old hump they first had several million years ago, when we used our feet to hang head downward from the limbs of trees while picking the scuppernong grapes, thorn plums, and bitter-sweet apples of those days.

OUT-OF-DOOR LIFE COMPELS TRAINING OF SENSES—"The best part of all human knowledge has come by exact and studied observation made through the senses of sight, hearing, taste, smell, and touch. The most important part of education has always been the training of the senses through which that best part of knowledge comes. This training has two precious results in the individual besides the faculty of accurate observation —one the acquisition of some sort of skill, the other the habit of careful reflection and measured reasoning which results in precise statement and record," says President Eliot in his admirable little book, "Changes Needed in American Secondary Education."

Chemistry and the engineering professions require the swift, sure reaction of the mind through the senses that the boy or girl can get only from self-reliant life, out of doors. City industrial life that limits children's play to the street, that brings them up in homes where heating, lighting, and cooking require only turning a valve, pressing a button, or opening a can, is not educational. It produces mental coma, especially when supplemented by such passive and vicarious sports as moving pictures, professional baseball, or riding to school in some one else's car.

Most of those in our profession who are over thirty were raised under the splendid educational influence of farm or village life. Their minds were activated in the fields and woods, and by doing, alone, the whole of a great variety of real tasks at home.

The younger ones of us, since telephone and trolley days, missed that training. It is unattainable to the youths who to-day are entering chemical and engineering industry, unless we more fortunate older men reorganize public education on its original foundation of the farm, the forest and the wide out of doors. At the beginning of the school year and of the autumn and winter seasons of civic activity, we can do no service of greater value than that of coöperating locally and nationally in practical work directed to that end.

MUCH OF THE ENERGY WE FORMERLY EXPENDED IN EXPLOITING THE VAST NATURAL RESOURCES OF OUR COUNTRY TO THEIR EXHAUSTION IS NOW BEING TURNED DESTRUCTIVELY AGAINST SOCIETY ITSELF—Continuance of profitable industry requires that we devise practical measures to bend that energy back to the land, in organized production of food and the raw materials of clothing and housing; and especially in attainment of education, drawn from farm and forest.

Accident Prevention through Education

The National Safety Council has so systematized accident prevention that most industrial plants of Council members protect their machines so well that it almost requires a professional burglar to break into them and get hurt. The result has been reduction of accidents by half, with some member companies reporting seventy per cent less accidents. The annual cost of accidents is therefore an approximate measure of the annual saving. On this assumption, using the figures of 1919, the net annual saving secured that year by safety devices is estimated to be one billion and some odd dollars; $1,014,000,000 to be exact. This total is reached after crediting $331,000,000, that need no longer be expended on the twenty-three thousand men killed that year in industry. The saving is a sum that compares favorably with the German reparation payments.

HOW DID THESE 23,000 MEN GET KILLED? We don't know about all of them. But we do know the details of several such deaths near home. In one case a workman dropped a jackknife, which skittered in under the main pulley. He deliberately climbed over, through and under a labyrinth of pipe and wire netting guards that surrounded that pulley. He did not get the jackknife, but he did get killed.

In another case, happily not fatal, a distillation kettle was set with its sampling nozzle pointed into a corner, in order that approach to it should be safe from both sides. The Young Chemist in charge, had occasion to try the oxidizing effect of potassium bichromate. He administered the dose through the sampling nozzle. But, in order to watch the effects more closely, in case there were an eruption, as was anticipated, our chemist got on the back side of the nozzle, up in the corner. He was a Cornell man, too.

He got his wish, for he both observed and experienced the effect. The blast from the nozzle destroyed a perfectly good pair of pants and burned an area on Young Chemist that kept him in bed several weeks. He and the charge in the kettle were thoroughly oxidized.

The men in these accidents and scores of others lacked gumption, and the primeval sense of self-preservation which self-reliant life out of doors compels. A mountain of guards would have been inadequate. The primitive instinct of self-preservation is slipping away from us, under the influence of specialized, industrial, city life. Legislation and legal precedent have passed the responsibility for one's safety over to the other fellow. If I go to sleep on the railroad track, the railroad must pay for the funeral and support my widow until death do us reunite or she marries again.

Here is one proof among many, of the tragic consequences of departing from nature, the farm, forest and stream, as the basis of education to train the senses, including common sense. "One of the best methods of developing the minds of children is practice in the coördinated activities of the brain and the hand," says President Eliot. "If brain, eye and hand are coöperating, the developing mental effect is increased; and the mental action and reaction is stronger still when eyes, ears and hands, and the whole nervous system, the memory and the discriminating judgment are at work together."

Camp life and country compel the child to experience that sort of action and reaction. City education cannot be molded to yield that result. In the accidents cited the victims lacked "discriminating judgment."

As a means of accident prevention to workmen, as a means of sharpening the observation and the reasoning powers of chemists, and as a basis of broader, deeper, sweeter life for all of us, we should restore nature, the out of doors, to the head of our public school curriculum.

Society of Chemical Industry

The program of the annual general meeting of the British Society of Chemical Industry, to be held at McGill University, Montreal, Canada, August 29 to 31, 1921, is as follows:

MONDAY, AUGUST 29

10:00 A.M.—Council meeting, McGill University.
11:00 A.M.—Annual meeting: (a) Address of Welcome. (b) Reply. (c) General business of the Society.
1:00 P.M.—Civic Reception and Lunch.
3:00 P.M.—Special visit to McDonald Agricultural College. Supper and Garden Party.

TUESDAY, AUGUST 30

10:30 A.M.—(a) Address. (b) Pulp and Paper Symposium (3 papers).
1:00 P.M.—Luncheon at Windsor Hotel given by Montreal Section.
3:00 P.M.—Visits to various industrial plants.
7:30 P.M.—Banquet, Windsor Hotel.

WEDNESDAY, AUGUST 31

10.00 A.M.—Special addresses and technical papers.
1:00 P.M.—Luncheon at Windsor Hotel, given by Montreal Section.
3:00 P.M.—Special Convocation at McGill University.
4:00 P.M.—Trip down Lachine Rapids.
11:55 P.M.—Leaving by night train to Shawinigan.

THURSDAY, SEPTEMBER 1

Shawinigan—Visits to Grand Mere and Shawinigan Falls Industries, under the auspices of Shawinigan Falls Section S. C. I.

FRIDAY, SEPTEMBER 2

Ottawa—Visits and entertainment, under auspices of Ottawa Section.

SATURDAY, SEPTEMBER 3

Toronto—Visits and entertainment, under auspices of Toronto Section.

SUNDAY, SEPTEMBER 4

Toronto—Visits and entertainment, and by boat to Niagara Falls, under auspices of Toronto Section.

MONDAY, SEPTEMBER 5

Niagara—Visits to Industries on Canadian and American sides.

SCIENTIFIC SOCIETIES

Chemistry's Greatest Rally

By John Walker Harrington

Chemistry comes into its own next month in New York at its greatest rally. Such is the prophecy justified by every wave of energy which radiates from those able catalysts, the Coördinating Committee, whoare bearing the burden and the heat of preparation these August days.

Their advices from Montreal show, for instance, that the first meeting which the parent organization, the Society of Chemical Industry of Great Britain, has ever held with its Canadian Section will bring to Montreal hundreds from beyond the Atlantic. When the sessions and the excursions are over in the Dominion, this overseas delegation, and many of the Canadian members, will cross the international border to meet in joint session with the American Chemical Society. In this company there will be probably four hundred; the American Section of the Society of Chemical Industry will add another large quota; while our own organization, with 2500 in the New York Section alone, and the representatives from other sections throughout the United States, should easily bring the registration to between three and four thousand. In such an assemblage as this, Anglo-Saxon chemistry will find a veritable apotheosis.

So important do the civil authorities regard this coming of the English-speaking chemists, that Governor Miller of New York will go in person to greet them at Niagara Falls and formally welcome them to American soil on Labor Day. With him will be a reception committee consisting of Mr. S. R. Church, chairman of the American Section of the Society of Chemical Industry; Professor Edgar F. Smith, president of the American Chemical Society; Dr. David Wesson, president of the American Institute of Chemical Engineers; Dr. Acheson Smith, president of the Electrochemical Society; and Professors Charles F. Chandler, Ira Remsen, and M. T. Bogert, and Dr. William H. Nichols, past presidents of the Society of Chemical Industry. They will be assisted by Mr. A. H. Hooker, the chairman of the Arrangement Committee at the Falls, and by Mr. E. G. Rippell, who has charge of the reception to be accorded to the distinguished visitors on their arrival that same day at Buffalo.

Gardiner & Son
Allen Rogers

Campbell Studio
J E. Zanetti

Otto Sarony
B. C. Hesse

Gardiner & Son
S. R Church

Coordinating Committee

A glance at the list of the foreign chemists suggests a "Who's Who" of science. At the head of the British Society is Sir William Pope, D.Sc., F.R.S., K.B.E., whose splendid work in industry with the Manchester Gas Corporation, and whose scientific achievements as professor of chemistry at the Universities of Manchester and Cambridge easily come to mind. Many who knew him in other years will meet him for the first time since he was made a Knight of the British Empire, in recognition of his researches through which his country was able enormously to increase the supply of mustard gas in the late war.

Other prominent figures in the party will be Dr. Louis A. Jordan, Chevalier of the Crown of Italy, who rose to new distinction as a member of the British Mission on Explosives to the Italian Government; Dr. Andrew Smith, managing director of the firm of Leech, Neal & Co. Ltd.; Dr. C. J. Goodwin, of Oscar Goodwin & Sons, explosives engineers; Dr. Frederick William Atack, who organized the publication of the "Chemists' Year Book;" Dr. Andrew McWilliam, one of the world's best-known steel metallurgists; Dr. C. S. Garland, pioneer manufacturer of thorium nitrate; and Dr. Frederic William Gamble, director of Allen & Hanbury's Ltd.

Among the noted Canadian chemists expected are: Dr. R. F. Ruttan, D.Sc., F.R.S., director of chemistry at McGill University; Dr. Milton L. Hersey, one of the founders and a past chairman of the Canadian Section of the Society of Chemical Industry; Mr. H. W. Matheson, chairman of the Montreal Section, S.C.I.; and Mr. Theodore H. Wardleworth, member of the General Committee and past chairman of the Canadian Section.

The visitors, coming from the meetings at Montreal, which begin on August 29, and having made stops at Toronto and Ottawa, and the tour of the industries at Grand Mère and Shawinigan Falls, will have seen chemical Canada in many phases before they reach the United States. From the time they leave Buffalo, however, after having been entertained there at dinner on the evening of September 5, they will be in many contacts with the chemistry of the United States. They will spend much of next day as the guests of the Solvay Process Company at Syracuse; leave in the mid-afternoon for Albany, embark there that night on a specially chartered steamboat for a trip down the Hudson River, and reach New York City early the next morning.

So interesting and so varied will be the journeys of these British and Canadian pilgrims of science, that they will be accompanied on both sides of the border by a large representation from "The States." As they are approaching the city, however, the thousands who are to attend the meetings of the American organizations will be coming from many directions.

Registration for the Fall Meeting of the American Chemical Society will begin at the Chemists' Club, 52 East 41st St., at nine o'clock on the morning of Tuesday, September 6. After

Tuesday, it will be at Earl Hall, Columbia University. The Council Meeting will be held at the Chemists' Club on Tuesday fternoon, to be followed by dinner.

Photo by Gessford

JOHN E. TEEPLE
CHAIRMAN, EXECUTIVE COMMITTEE

As indicated on the preliminary program, just issued from the office of Secretary Parsons, the General Meeting of the American Chemical Society in the gymnasium at Columbia University at ten o'clock on the morning of September 7 will be attended by such of the foreign delegation as may have made the portage from the pier to the heights of Morningside. There they will be welcomed at a luncheon for the British and Canadian visitors given by the American Section of the Society of Chemical ndustry. A more extended opportunity for the American hemists to meet them will be offered at the reception and awn party to be given on the campus of Columbia Univerity in the afternoon at four o'clock, while that evening the merican Chemical Society will entertain the guests at a smoker rranged at the Waldorf-Astoria, its official hotel headquarters. t the same place, the customary banquet of the Society vill be held on the evening of Thursday, September 8, losely following the international meeting which has been rranged for the afternoon at the College of the City of New York. Ample accommodations have been provided in Haveneyer and Engineering Halls of Columbia University for the neetings of the various sections and divisions of the American Chemical Society, to which the chemists from other lands ave been bidden. The Public Meeting will be addressed by President Smith on the evening of Friday, September 9. The ast day of the program is to be given to excursions to various lants and chemical industries in New York City and icinity.

Such are the high lights of what promises to be the largest and nost important gathering in the history of the American Chemical Society and of American chemistry. It represents a rally of ndustry at a time when chemists of the English speaking races are aking counsel together over the many post-war problems which nust be solved in the course of the next few months. Varied as re the social features of this great gathering, the scientific proram will have come to the fore with compelling interest. All f the divisions and sections will have two full days at their disosal. Among the special features of the scientific session will be he symposiums on filtration and on gas chemistry under the uspices of the Division of Industrial and Engineering Chemistry; symposium on vitamines by the Division of Biological Chemisry; the Cellulose Section's symposium on cellulose esters, and the ymposium of the Petroleum Section on the emulsification roblems which confront that industry. Those who have conributions to the chemistry as well as to the application of dyes vill find much to interest them in the proceedings of the Dye Division. The Leather Section, which will have several noted eather chemists from abroad to address it, has already twentyive papers in hand. A new note will be added also by the first ession of the Section on Chemical Education, the organizing of which has been authorized for the New York Meeting.

Reservations are being made rapidly at the leading hotels of the city and members are also taking advantage of the exceptional opportunities for convenient and moderate priced lodgings to be had at the dormitories near Columbia University.

Days after the meetings and excursions are over, however, there will still be chemists galore in New York, for many will remain to attend the Seventh National Exposition of Chemical Industries at the Eighth Coast Artillery Armory in the Bronx, which will open on September 12 and close with the week. Two booths have been retained by the American Chemical Society and its Advertising Department and will be used as a social center for members and their guests during the Exposition. In view of the presence of so many scientists from Great Britain and Canada, the Exposition will have an international tone such as that which will pervade the entire Fall Meeting, and will be an appropriate finale of America's great rally of applied chemistry.

. . . .

CHAIRMEN OF LOCAL COMMITTEES

Executive Committee: JOHN E. TEEPLE
Coördinating Committee: B. C. HESSE
Registration Committee: H. R. MOODY
International Meeting Committee: CHAS. BASKERVILLE
Publicity Committee: CHAS. H. HERTY
Transportation Committee: C. F. ROTH
Information, Marshals, and Guides Committee: H. G. CARRELL
Hotels Committee: CHAS. F. LINDSAY
Banquet Committee: F. G. ZINSSER
Printing Committee: F. M. TURNER, JR.
Smoker Committee: K. G. MACKENZIE
Excursions Committee: J. V. N. DORR
Columbia Dormitories Committee: R. H. MCKEE
Ladies Entertaining Committee: MRS. L. H. BAEKELAND

Other members of the Executive and Coördinating Committees: MARTIN H. ITTNER, HERBERT G. SIDEBOTTOM, C. A. BROWNE, D. W. JAYNE, J E. ZANETTI, S. R. CHURCH, ALLEN ROGERS.

. . . .

REDUCED RAILROAD RATES

The Trunk Line Association and the Southeastern Passenger Association have granted the AMERICAN CHEMICAL SOCIETY for its September meeting special rates of fare-and-a-half on the certificate plan, but on account of the fact that Labor Day falls on September 5 such rates cannot be secured on tickets bought before September 6. Members coming for the meeting may purchase their tickets on September 6, 7, 8, and 9, on which days they may use them for passage. Identification certificates upon which railroad tickets will be sold will be supplied to members of the respective societies upon request to C. L. Parsons, secretary, American Chemical Society, 1709 G St., N. W., Washington, D. C., or to Allen Rogers, secretary, American Section, Society of Chemical Industry, Pratt Institute, Brooklyn, N. Y.

Immediately upon arrival in New York members should hand their certificates in at the Registration Desk in order to be validated. They may secure these tickets for return passage on the 9th and 10th, but the return ticket will be good for use up to and including September 23, thereby giving the members the opportunity of attending the Seventh National Exposition of Chemical Industries.

This fare rate on the certificate plan is granted only upon the certification of 350 certificates. It is therefore very necessary that every chemist leaving his home town on September 6, 7, 8, or 9 should request a certificate for the meeting of the American Chemical Society.

This reduced fare on the certificate plan is also extended to the Society of Chemical Industry.

Arrangements have been made by the Transportation Committee for a train of Pullman cars to leave Buffalo during the night of September 5 and 6, probably leaving Buffalo early in the morning of the 6th, going direct to Syracuse for the visit to the Solvay plants. In the afternoon the train will proceed to Albany, there to make connection with the Hudson Navigation Company, Steamer "Berkshire," upon which reservations for

150 persons have been made for the night voyage down the river. Any members of the Society coming from Buffalo and desiring accommodations on this train should notify the chairman of the Transportation Committee, Charles F. Roth, Room 707, 342 Madison Ave., New York City. For members returning by the same route the special fare upon the certificate plan will apply.

The Chemical Exposition

The coming Seventh National Exposition of Chemical Industries promises to be the forerunner of big business for the chemical industry and is to be known as the Prosperity Exposition. Considerable and wide interest is being shown in the Exposition; so much, in fact, that the managers have been obliged to prepare a broadside sheet to respond to the inquiries made of them regarding the exhibits.

Among the additional technical papers is one on the Crushing, Grinding and Pulverizing program entitled "The Development of Compound Grinding Mills," by H. Schifflin of the Allis-Chalmers Mfg. Co.

Wallace Savage will be chairman of the Evaporating and Drying program; R. C. Beadle, editor of *Combustion*, of the Power Plant in the Chemical Industries program; and R. S. Perry, of the Paint and Varnish Industry meeting.

Three papers on the Power Plant in the Chemical Industries are as follows:

Compressed Air Installation in Industrial Plants. A R Stevenson, Jr , General Electric Co.

The Application of Power in Electrochemical Industries. D. B. Rushmore, J. A. Seede and E. Pragst, General Electric Co.

A New Method for Coking Coal as Required for Industrial Fuel. D. S. Chamberlin, Fuel Distillation Industries, Inc.

An additional paper on Industrial Problems is "Material Handling in Industrial Plants," by R. H. McLain of the General Electric Co.

Papers dealing with the Paint and Varnish Industry, to be given on the afternoon of Thursday, September 15, are as follows:

Reflection Factors on Industrial Paints. H. A. Gardner, Institute of Paint and Varnish Research.

Laboratory Control. L. P. Nemzck, du Pont de Nemours & Co.

Paint and Varnish Waste Control. R. S. Perry, Perry and Webster, Inc

Rust: Its Cause and Prevention. Maximilian Toch, Toch Bros.

Physical Testing of Paints and Paint Materials. Frank G. Breyer, New Jersey Zinc Co.

The Ideal Paint and Varnish Specification. F. P. Ingalls, John W. Masury and Co.

Limitations of Standardization of Paint and Varnish Manufacture. D. A. Kohr, Lowe Bros. Co.

At the evening session, the following papers will be followed by eight reels of pictures on this industry, furnished by six manufacturers:

Save the Surface and You Save All with Paint and Varnish. Ernest T. Trigg, *chairman*, "Save the Surface" Committee, Paint Manufacturers' Association of the United States.

What Is Paint? G. P. Heckel, *secretary*, Paint Manufacturers' Association of the United States.

Several additional motion pictures are listed on the program These include:

Du Pont Dyes—Their Manufacture. (2 reels) Courtesy of du Pont de Nemours & Co.

The Story of Armco Ingot Iron. (3 reels) Courtesy of American Rolling Mill Co.

Modern By-Product Coking. (2 reels) Courtesy of The Koppers Co

Reagent Chemicals. I—Proposed Specification for Sulfuric, Nitric, and Hydrochloric Acids, and for Ammonium Hydroxide[1,2]

By W. D. Collins

Chairman of Committee on Guaranteed Reagents and Standard Apparatus

The specifications given below are intended to serve as standards for reagents for use in careful, general analytical work. The limits for strength and purity are nearly all taken from published works on the testing of reagents or from labels or statements of manufacturers. Records of tests of reagents of various makes over a number of years indicate that the requirements have been met very generally in the past.

Two kinds of limits are set. The first is an actual limit, such as the strength of a reagent. This is a definite quantity and can be determined accurately in a number of ways. It seems unnecessary to specify details for determinations which are described in all standard texts and which permit many variations without loss of accuracy. Other requirements depend upon the method of testing and the limit is the quantity of the impurity which will give the test. This is not so definite and is given in parenthesis after the statement that the reagent is to pass the test given. In these instances the test must be described in detail since it defines the limit.

The expression "none" has not been used, and "trace" only for pyridine in ammonium hydroxide. The committee did not have any quantitative method which would serve to measure the small quantity of pyridine in reagent ammonium hydroxide. "None" as used on some labels requires definition. If the definition is that the reagent shall not respond to a given test which is not very sensitive, the quantity of impurity permitted may interfere seriously with the use of the reagent for certain purposes. "Trace" is even more unsatisfactory as a limit for an impurity which may be determined quantitatively without excessive work.

The use of specifications in purchasing requires judgment and no attempt has been made to prepare specifications which would not be subject to abuse by incompetent buyers who depended on unskilled analysts. The testing of reagents is not simple, and it is not believed that directions can be so written that they cannot be misunderstood. Any lack of equipment or experience must be taken into consideration in applying the specifications and tests, and allowance must be made for errors which may result from these causes.

Comments on these specifications are desired so that if necessary they may be modified to represent more accurately the standards for reagents desired by the American Chemical Society, and may serve as a pattern for specifications for other reagents.

Proposed Specification for Reagent Sulfuric Acid

Requirements: The material desired under this specification is a high-grade concentrated sulfuric acid suitable for use as a reagent in general laboratory work. The acid shall conform to the following requirements:

Appearance—Colorless, and free from suspended or insoluble matter when received, and after diluting to 2 *N* concentration.

Acidity—Not less than 93 per cent by weight of H_2SO_4

Nonvolatile Matter—Not more than 0 0005 per cent.

Chloride (*Cl*)—To pass test given below (not more than 0.00006 per cent).

Nitrate (NO_3) -To pass test given below (not more than 0 0002 per cent).

Ammonium (NH_4)—To pass test given below (not more than 0.0005 per cent).

Substances Oxidizable by Permanganate—To pass test given below (not more than 0.0005 per cent as SO_2).

Arsenic (*As*)—Not more than 0 000003 per cent.

Tests: Samples shall be tested by the following methods:

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities.

Appearance—Mix the material in original container and pour 10 cc. into a test tube (150 mm by 20 mm.) Compare with distilled water in a similar tube. The solutions should be equally clear and free from suspended matter, and on looking across the columns by transmitted light there should be no apparent difference in color between the two solutions. Dilute a portion of the acid with water until 2 *N*, and compare as before. No difference in turbidity should be observed.

Acidity—Titrate a weighed portion of the acid, after suitable dilution, with 0.5 *N* sodium hydroxide solution, using methyl orange as indicator.

Nonvolatile Matter—Evaporate 55 cc. of the acid to dryness in platinum, ignite at cherry redness for 5 min., cool, and weigh. The residue should not weigh more than 0.0005 g.

Chloride—Dilute 5 cc. of the acid with an equal volume of water and

---

[1] Received June 24, 1921.

[2] Supplementary to the Report of the Committee on Guaranteed Reagents and Standard Apparatus, This Journal, 13 (1921), 402.

cool Add 1 cc of silver nitrate solution (2 g $AgNO_3$ in 100 cc.). The turbidity should not be greater than that produced by 0.005 mg. of chloride (Cl) as sodium chloride (NaCl) in 9 cc. of water to which are added 1 cc. of dilute nitric acid (1 volume concentrated acid diluted to 10) and 1 cc. of silver nitrate solution (2 g $AgNO_3$ in 100 cc).

Nitrate—Dilute a sample of the acid with an equal volume of water and overlay 10 cc. of the cooled liquid upon diphenylamine solution (0.5 g. in 100 cc. sulfuric acid and 20 cc. water). A blue color should not appear at the zone of contact within one hour.

Ammonium—Dilute 6 cc. of the acid with 90 cc. of water, render alkaline with sodium hydroxide, and add 1 cc. of Nessler's reagent. No more color should develop than is caused by 0.05 mg. NH_4 in the same volume of water with the quantities of sodium hydroxide and Nessler's solution used n the test.

Substances Oxidizable by Permanganate—Dilute 20 cc. of the acid with 60 cc. of water, cool to 25° C., and add 0.05 of 0.1 *N* potassium permanganate. The mixture should remain pink for not less than 5 min.

Arsenic—Add 3 cc. of concentrated nitric acid to 100 g. of the acid and evaporate to about 10 cc. Cool, dilute the residue with 40 cc. of water, and determine arsenic by the Gutzeit or the Marsh-Berzelius method. A second or third evaporation to fumes after dilution may be necessary to remove all of the nitrate. Special care in making blank tests is necessary n this determination.

PROPOSED SPECIFICATION FOR REAGENT NITRIC ACID

REQUIREMENTS: The material desired under this specification is a high-grade concentrated acid suitable for use as a reagent in general laboratory work. The acid shall conform to the following requirements:

Appearance—Colorless and free from suspended matter or sediment.

Acidity—Not less than 68 per cent by weight of HNO_3.

Nonvolatile Matter—Not more than 0.0005 per cent.

Sulfate (*SO_4*)—To pass test given below (not more than 0.0002 per cent).

Chloride (*Cl*)—To pass test given below (not more than 0.00007 per cent).

Iodate and Iodide (*as I*)—To pass test given below (not more than 0.0001 per cent).

Arsenic (*As*)—Not more than 0.000003 per cent.

TESTS: Samples shall be tested by the following methods:

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities.

Appearance—Mix the material in original container and pour 10 cc. into a test tube (150 mm by 20 mm.), and compare with distilled water in a similar tube. The solutions should be equally clear and free from suspended matter, and on looking across the columns by transmitted light there should be no apparent difference in color between the two solutions.

Acidity—Titrate a weighed portion of the acid, after suitable dilution, with 0.5 *N* sodium hydroxide solution, using methyl orange as indicator.

Nonvolatile Matter—Evaporate 70 cc. of the acid to dryness in platinum, ignite at cherry redness for 5 min., cool, and weigh. The residue should not weigh more than 0.0005 g.

Sulfate—Add 0.01 g. sodium carbonate to 20 cc. of the acid, evaporate to dryness, take up with water, filter, and make up to a volume of 10 cc. in a test tube. Add 1 cc. hydrochloric acid (1 volume strong acid in 20) and 1 cc. barium chloride solution (10 g. $BaCl_2.2H_2O$ in 100 cc.). The turbidity after 10 min. should not be greater than is obtained in an equal volume of distilled water containing 0.01 g. sodium carbonate neutralized with hydrochloric acid, 0.05 mg. of sulfate (SO_4), and the quantities of hydrochloric acid and barium chloride used with the sample.

Chloride—Dilute 5 cc. of the acid with an equal volume of water and add 1 cc. of silver nitrate solution (2 g. $AgNO_3$ in 100 cc.). The turbidity should not be greater than that produced by 0.005 mg. of chloride (Cl) as sodium chloride (NaCl) in 9 cc. of water to which are added 1 cc. of dilute nitric acid (1 volume concentrated acid diluted to 10) and 1 cc. of silver nitrate solution (2 g. $AgNO_3$ in 100 cc.).

Iodate and Iodide—Dilute 25 cc. of the acid with 25 cc. of water, add about 0 5 g. of zinc and a few cc. of chloroform, and shake well. The chloroform should not acquire a violet color.

Arsenic—Mix 100 g. of the acid with 5 cc. of sulfuric acid, evaporate until fumes are evolved, cool, and determine arsenic by the Gutzeit or the Marsh-Berzelius method. A second or third evaporation to fumes after dilution may be necessary to remove all nitrate. Special care in making blank tests is necessary.

PROPOSED SPECIFICATION FOR REAGENT HYDROCHLORIC ACID

REQUIREMENTS: The material desired under this specification is a high-grade concentrated hydrochloric acid suitable for use as a reagent in general laboratory work. The acid shall conform to the following requirements:

Appearance—Colorless and free from suspended matter or sediment.

Acidity—Not less than 35 per cent by weight of HCl.

Nonvolatile Matter—Not more than 0.0005 per cent.

Sulfate (*SO_4*)—To pass the test given below (not more than 0.0002 per cent).

Free Chlorine (*Cl*)—To pass the test given below (not more than 0.0002 per cent).

Sulfite (*SO_3*)—To pass test given below (not more than 0 003 per cent).

Arsenic (*As*)—Not more than 0.00001 per cent.

Iron (*Fe*)—Not more than 0.0001 per cent.

TESTS: Samples shall be tested by the following methods:

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities.

Appearance—Mix the material in original container, pour 10 cc. into a test tube (150 mm. by 20 mm.), and compare with distilled water in a similar tube. The solution should be equally clear and free from suspended matter, and on looking across the columns by transmitted light there should be no apparent difference in color between the two solutions

Acidity—Titrate a weighed portion of the acid, after suitable dilution, with 0.5 *N* sodium hydroxide solution, using methyl orange as indicator.

Nonvolatile Matter—Evaporate 85 cc. of the acid to dryness in platinum after addition of a drop of sulfuric acid, ignite at cherry redness for 5 min., cool, and weigh. The residue should not weigh more than 0.0005 g.

Sulfate—Add 0.01 g. sodium carbonate to 20 cc. of the acid, evaporate to dryness, take up with water, filter, and make up to a volume of 10 cc. in a test tube. Add 1 cc. hydrochloric acid (1 volume strong acid in 20) and 1 cc. barium chloride solution (10 g. $BaCl_2.2H_2O$ in 100 cc.). The turbidity after 10 min. should not be greater than is obtained in an equal volume of distilled water containing 0.01 g. sodium carbonate neutralized with hydrochloric acid, 0.05 mg. of SO_4, and the quantities of hydrochloric acid and barium chloride used with the sample.

Free Chlorine—To 100 cc. of the sample add 100 cc. of water and cool; add 6 drops of 2 per cent potassium iodide solution and 1 cc. of carbon disulfide, and mix. The carbon disulfide should not acquire a pink color. The potassium iodide should be free from iodate.

Sulfite—Add 0.05 cc. of 0.1 *N* iodine solution and a few drops of starch solution to 50 cc. of water, and then add 5 cc. of the sample previously diluted with 50 cc. of water. The mixture should retain a blue color after mixing.

Arsenic—Determine on 20 cc. of the sample by the Gutzeit or the Marsh-Berzelius method. Special care in making blank tests is necessary in this determination

Iron—To 100 cc. of the sample add about 0.05 g. of potassium chlorate and 2 drops of sulfuric acid (1 part strong acid in 4) and evaporate to a volume of about 2 cc. Wash into a color comparison tube, add 2 cc. of 5 per cent ammonium thiocyanate solution, and stir well. Compare with a solution similarly prepared and diluted to the same volume to which standard ferric chloride solution is carefully added from a buret until the tints match.

PROPOSED SPECIFICATION FOR REAGENT AMMONIUM HYDROXIDE

REQUIREMENTS: The material desired under this specification is a high-grade concentrated ammonia water suitable for use as a reagent in general laboratory work. The material shall conform to the following requirements:

Appearance—Colorless and free from suspended matter or sediment.

Strength—Not less than 28 per cent by weight of NH_3.

Nonvolatile Matter—Not more than 0.005 per cent.

Carbon Dioxide (*CO_2*)—To pass test given below (not more than 0.008 per cent).

Total Sulfur (*as SO_4*)—To pass test given below (not more than 0.0003 per cent).

Chloride (*Cl*)—To pass test given below (not more than 0.00005 per cent).

Pyridine—To pass test given below (not more than a trace).

TESTS: Samples shall be tested by the following methods:

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities.

Appearance—Mix the material in original container and pour 10 cc. into a test tube (150 mm. by 20 mm.), and compare with distilled water in a similar tube. The solutions should be equally clear and free from suspended matter, and on looking across the columns by transmitted light there should be no apparent difference in color between the two solutions.

Strength—Titrate a weighed portion of the sample, after suitable dilution, with 0 5 *N* acid solution, using methyl orange as indicator.

Nonvolatile Matter—Evaporate 100 cc. of the sample to dryness, ignite, cool, and weigh. The residue should not weigh more than 0.0045 g.

Carbon Dioxide—Transfer 15 cc. of the sample to a 100-cc. flask that has been swept free from CO_2, and add at once 50 cc. of clear calcium hydroxide solution Cover with a watch glass and boil 5 min. At most only a slight turbidity should appear.

Total Sulfur—To 20 cc. of the sample add 0.01 g. sodium carbonate and evaporate to 5 cc. Add a drop of bromine water (or sufficient to impart a slight color to the solution) and evaporate to dryness, take up in a slight excess of dilute hydrochloric acid, and again evaporate to dryness. Take up in a few cc. of water, filter, and make to a volume of 10 cc. in a test tube. Add 1 cc. of dilute hydrochloric acid (1 volume of strong acid in 20) and 1 cc. of barium chloride solution (10 g. $BaCl_2.2H_2O$ in 100 cc.). The turbidity produced after 10 min. should not be greater than is obtained in an equal volume of distilled water containing 0.01 g. sodium carbonate neutralized with hydrochloric acid, 0.05 mg. of SO_4, and the quantities of hydrochloric acid and barium chloride used with the sample.

Chloride—To 10 cc. of the sample add 0.005 g. of sodium carbonate and evaporate to dryness. Take up with 8 cc. of water, and add 1 cc. of dilute nitric acid (1 volume concentrated acid diluted to 10) and 1 cc. of silver nitrate solution (2 g. $AgNO_3$ in 100 cc.). The turbidity should not be greater than that produced by 0.005 mg. of chloride (Cl) as sodium chloride

(NaCl) in 8 cc. of water to which have been added the quantities of nitric acid and silver nitrate used with the sample.

Pyridine—Dilute 25 cc. of the sample with 25 cc. of water and nearly neutralize with about 25 per cent sulfuric acid, using methyl orange as an indicator. Stir briskly and note the odor. No more than a very faint odor of pyridine should be obtained.

Membership Directory of the Society

The 1921 Directory of the membership of the American Chemical Society is now being printed and will shortly be off the press and ready for distribution under the following regulations adopted by the Council:

A—A single copy of the list may be sent gratuitously to:

(1) Regular advertisers in our publications but only for their own use.

(2) Officers or committees of the Society for Society purposes.

(3) Other scientific, benevolent or educational societies in exchange for their own list when same is desired.

B—On payment of $1.00 to cover the cost of printing and mailing it may be sent to any member of the Society on signed application therefor stating that the member desires it for his own personal use and that he will not loan or dispose of it to any firm or to any other individual to be used for advertising purposes.

Charles L. Parsons, *Secretary*

Calendar of Meetings

American Pharmaceutical Association—Sixty-ninth Annual Meeting, Hotel Grunewald, New Orleans, La., week of September 5, 1921.

American Chemical Society and Society of Chemical Industry—New York, N. Y., September 6 to 10, 1921.

Seventh National Exposition of Chemical Industries—Eighth Coast Artillery Armory, New York, N. Y., September 12 to 17, 1921.

American Institute of Mining and Metallurgical Engineers—Fall Meeting, Wilkes-Barre, Pa., September 12 to 17, 1921.

American Electrochemical Society—Fall Meeting, Lake Placid, N. Y., September 29 to October 1, 1921.

Technical Association of the Pulp and Paper Industry—Fall Meeting, Washington, D. C., Philadelphia, Pa., Spring Grove, York, York Haven, Pa., and Wilmington, Del., October 18 to 20, 1921.

THE SECOND INTERNATIONAL CHEMICAL CONFERENCE

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

The Second International Conference of Pure and Applied Chemistry met at Brussels, June 25 to 30, 1921, under the presidency of Prof. Charles Moureu, member of the Institute de France and president of the International Union of Pure and Applied Chemistry.

The delegates were: Charles Moureu, *president*, Sir William Pope and Messrs. F. G. Cottrell, Emanuele Paterno and F. Swarts, *vice presidents*, Mr. Jean Gerard, *secretary*, Messrs. Biilmann, Moles, Mourelo, Conant, Mackall, Behal, Bordas, Kestner, Lindet, Lowry, Miall, Zenghelis, Nasini, Bertrand, Halvorsen, Holleman, Kruyt, de Trepka, Minovici, Schmitz, Guye, Votocek, Goslino, and Zega.

All the meetings were held at the Palais des Academies, which had been put at the disposal of the Union.

The order of the day consisted of meetings of the Council of the Union and its General Assembly. At the conference in Rome, last year, a number of committees were appointed, and the reports of their work during the past year served as a basis for the discussions at the present conference.

After a warm welcome from the members of the Belgian Chemical Society, the Council met to consider new requests for admission and to arrange for the general meeting. The General Assembly which followed approved the action of the Council, as well as the financial report for the past year. Then the Conference, with its new members, took up the study of the subjects on the order of the day.

The first general meeting was devoted to organization and to the appointment of committees to examine the reports, and the later meetings were devoted to the discussion of the conclusions reached by the committees. The resolutions passed were of such importance as to warrant the inclusion of their substance in this account of the conference.

In regard to the organization of the committee on atomic weights, it was decided that the old committee should be enlarged and renamed the Committee on Chemical Elements, and that, in addition to atomic weights, it should fix numerical data in the field of radioactivity. This plan was presented by Mr. Guye.

The report of the committee on nomenclature, which was presented by Mr. Marquis and was unanimously accepted, involved the appointment of three international committees on nomenclature: in organic, inorganic, and biological chemistry. Each of these committees would include a member from every country belonging to the Union. There would be appointed, further, three working committees of six members each, chosen by the international committees. The duty of each member of the working committees would be to establish, with the aid of his national organization, a national committee for the discussion of questions of nomenclature. The proposals of the national committee would be collected in a report to be transmitted by the member of the working committee to his colleagues from the other nations. The nations not represented on the working committees would be invited to make their suggestions to any member of the active committee concerned. The members of the working committee would meet annually to confer, and to submit definite proposals to the international committee.

The following motion on bibliographic abbreviations was adopted on the proposal of Mr. Guye:

> The committee resolves that after agreement with the American Chemical Society the Bureau of the Union should institute an inquiry among the federations and national councils. This inquiry would have for its object to find out whether the principal chemical periodicals should be disposed to accept the system of abbreviations to which the majority should agree. The result of this inquiry would be communicated to the 1922 meeting of the Union, which would take definite steps with a clear knowledge of their probable extent.
>
> It is, of course, evident that a general measure would not be of use unless the great majority of periodicals agreed to it.

Dr. Pondal, in the name of the Chemical Society of Argentina, offered to guarantee the expense of the proposed inquiry, and the Council accepted this offer.

On the question of the unification of chemical abstracts, which had already been the subject of preliminary conferences in London and Brussels, in 1919, the Conseil National des Pays-Bas presented the following report of their conclusions:

> 1—That the Bureau of the International Union should take the initiative in assembling representatives of the various chemical periodicals publishing abstracts, with a view to opening the discussion of the eventual creation of a central publication, and the defraying of expenses connected with such a publication, conforming to the action taken by the Conseil National des Pays-Bas.
>
> 2—That the possibility be considered of establishing an international chemical bulletin, as proposed by Messrs. Kling and Lassieur, which the the committee considers of undoubted value, and that the cost of the establishment and maintenance of such a bulletin be considered.

The Assembly adopted the following conclusions on the International Institute of Chemical Standards, as presented by Mr. Timmermans:

> 1—To avoid confusion which might interfere with the work of the three sections which make up the Institute, the Conference decided that the following names shall be used:

Bureau of Physicochemical Standards, with headquarters at Brussels.

Pure Products for Research, in England.

Review Service on Industrial and Technological Products, at Paris.

2—The national committee of each country affiliated with the Union is invited to appoint from its members a correspondent for each of the three sections, through whom they may consider officially all questions which may rise.

3—To permit as rapid as possible a realization of the objects of the Bureau of Physicochemical Standards, the Conference requests the Council of the Union to provide for the Bureau an annual income of ten thousand francs.

The report presented by Mr. Swarts, for the committee on the establishment of a thermochemical standard, was as follows:

The committee resolves that the scientists who publish thermochemical work shall indicate the substance which has served as the calorimetric standard.

The committee believes that methods of determining the heat of combustion of a substance chosen as standard should be discussed in an independent report.

No decision was reached in the matter of international patent. The committee was reappointed until the next meeting.

The order of the day involved three questions in applied chemistry. The report of the committee on industrial hygiene, presented by Mr. Carelli, was as follows:

The committee, composed of Mr. Caseneuve, *president*, and Messrs. Biilmann, Bosshard, Miall, Pomilio, Schmitz, Treub, and Carelli, has obtained a lengthy report, written by Prof. Pietro Biginelli, Chemical Inspector General of the Department of Public Health of Rome, and Prof. Giovani Loriga, Medical Inspector General of Industry and Labor. After examining this report, which surveys the chemical industries from the point of view of general hygiene, the committee has decided to modify its name. It believes it wise to consider "the chemical industry in its relation to public hygiene," and not to limit its study to industrial hygiene.

The Italian investigators, pointing out the ends proposed by legislations as to industrial hygiene, set forth very clearly the special position of the chemical industry as compared with other industries. The chemical industries are concerned with the hygiene of their surroundings as well as of their workers. The report enumerates the dangers which can be occasioned by the chemical industries, and points out that the solution of these problems is expressed largely by general formulas.

The committee recognizes, with its Italian confreres, that in the chemical industries hygiene demands a supervision of a technical character, involving on the one hand the skill of the engineer, and on the other the special training of the chemist. The task of the medical hygienist, on the other hand, is well defined and has become considerable.

The committee, while agreeing to the general conclusions of the report, believe that the following supplementary conclusions may be added:

The committee considers that there should be given, by means of courses of instruction in the higher schools, to physicians as well as to chemists and engineers, the instruction necessary to a proper appreciation of the questions of hygiene belonging to industry in general, and to the chemical industry in particular.

Finally, your committee, in common with the Italian investigators, believe that an organization for information as to all that is being done and all that should be done in industrial hygiene would be very useful in making popular the means of protection in the interests of the workers as well as in that of the neighborhood of the factory. The committee believes that, to accomplish this end as soon and with as little expense as possible, they could make use of the *Revue internationale d'hygiène publique*, founded by the league of Red Cross Societies at Geneva in 1920. This *Revue* provides original articles and also a critical review of the hygienic movement in all its branches. Beside the articles which bear on epidemiology there are others which deal with industrial hygiene, and which are concerned with protective prevention or with the hygienic supervision of industrial surroundings. This *Revue* might, by means of a subsidy, the amount of which should be determined and subscribed by the nations interested, be published more frequently, as a monthly rather than a bimonthly. It would thus become an international organ for all civilized nations, and could review the special publications of each chemical industry, thus bringing their work to popular attention.

The committee would like the Bureau to get into communication with the directors of the *Revue* at Geneva to formulate and solve all questions of the financing necessary for the realization of the project.

The principle of the creation of national and international laboratories for the study of ceramic products and fuels was decided on the proposal submitted by Mr. Pictet:

The preparatory committee in charge of the preliminary work relative to the establishment of national and international laboratories for the study of ceramic products and fuels is unanimously of the opinion that a national laboratory should be established in every country of the Union for the study of fuels. The work of these laboratories would naturally cover all questions connected with fuels, their nature, composition, transformations, and utilization.

The committee is equally unanimous in approving the creation of research laboratories for ceramic products. But, on account of the frequent connection of fuel problems with those of the industrial furnace, it would seem possible and desirable to study the questions relative to ceramics or refractory products as a special section of the fuel laboratories. This would avoid the probably insurmountable financial difficulties which would arise if the attempt were made to establish distinct research laboratories for refractory products.

A permanent committee was appointed, consisting of Messrs. Bone, Bordas, Etienne, Evans, Huybrechts, Kling, Lecrenier, Levi, Peny, Pictet, van Hutten, and Schmitz.

Finally, the report of Mr. Charles Marie on the tables of constants was adopted, and its author was warmly congratulated for the zeal which he displayed in bringing about the publication of this valuable document.

The Conference chose France as the meeting place for the Third International Conference of Pure and Applied Chemistry.

As is evident, the work of the Conference at Brussels was most profitable, and the results obtained were of extreme importance. The task of the delegates was greatly facilitated by the excellent organization of the Conference, in charge of Mr. Dony-Henault.

The Belgian government and manufacturers had combined in the welcome, charming the delegates with visits and most cordial receptions. Mr. Jules Destrée invited them to the Ministry of Arts and Sciences, where Mme. Destrée graciously extended to them the honors of her home. Mr. Solvay, whose solicitude for the chemists was lacking in no particular, had arranged a visit to his estate at Hulpe. Mr. Baudouin also entertained the delegates at the refinery at Tirlemont and at his estate at La Meck. Finally, the Belgian National Chemical Council gave a banquet, at which the president of the Union and Sir William Pope, in the name of the various delegations, thanked our Belgian friends for the charming reception which all had received at Brussels at this second conference.

Chemical Control Committee, National Fertilizer Association

The report of the Chemical Control Committee, presented at the recent meeting of the National Fertilizer Association, contained the following paragraphs:

The consensus of opinion expressed at the A. O. A. C. meeting indicates that borax is a trouble of the past. Only a few samples of fertilizer have been reported over the borax tolerance. No detrimental residual effects were observed in 1920 on fields badly damaged by borax in 1919. Methods for borax determination are now standardized and no further trouble from this source should ever develop. Further analytical coöperative work is being done under direction of the referee in order to prove definitely the reliability of the methods.

Inasmuch as the du Pont nitrometer is only applicable to inorganic nitrates and mixed acid and only approximate results are obtained, the referee recommended that work on this method be dropped. This was approved. It was further recommended and approved that the DeVarda alloy method for nitric and nitrous acid fertilizers be studied.

Further study of the neutral ammonium citrate solution was recommended and approved. The fact that the official method discriminates in the determination of phosphoric acid available in high-grade precipitated phosphates was developed by the referee and recommendations for further study were approved.

Great publicity has been given in the newspapers and technical journals to the pyrolytic method for volatilizaton of phosphoric acid from phosphate rock, as worked out by scientists of the Bureau of Soils at the Arlington Experimental Station. Whether or not this process is commercially practical for the fertilizer industry is yet to be demonstrated.

According to recent reports from Germany, Dr. Nathan Van Stone, a Chicago chemist, has been sentenced to four months' imprisonment by the criminal court at Frankfort. Dr. Van Stone was arrested on a charge of attempting to bribe a chemist of the Badische Aniline and Soda factory at Ludwigshafen into betraying factory secrets.

WASHINGTON LETTER

By Watson Davis, 1418 Rhode Island Ave., Washington, D. C.

The Fordney Tariff Bill

Tariff, particularly tariff on chemicals and dyestuffs, is occupying the attention of Congress at the present time. The permanent tariff bill is now being considered by the House, and, under the five-minute rule, the items on dyestuffs and control of dye importations are about to be discussed, along with hides, petroleum, cotton, and asphalt.

The Fordney tariff bill is the result of more than half a year's work on the part of the Ways and Means Committee, and it is still subject to change, both in the House during the next few days, and later in the Senate. It may be another half year before the measure is passed.

Of principal chemical interest is the embargo provided for the protection of American dyes and intermediates, pharmaceuticals, and other coal-tar products. This section of the bill provides that for three years dyes and other coal-tar chemicals manufactured in this country, and which are obtainable here on reasonable terms as to quality, price and delivery, cannot be imported under any conditions, while a total of six months' supply or less of those chemicals not available here can be brought into the country only by importers registered with the U. S. Tariff Commission. This is somewhat similar to the embargo proposed in the emergency act, but that was replaced by an extension of the licensing system now in use. Under the proposed act the United States Tariff Commission would administer the control provided.

The chemical schedule is more scientific and in more exact correspondence with commercial usage than any chemical schedule of previous tariff acts, owing to the fact that Representative Longworth of Ohio, who, with Representatives Copley of Illinois and Hadley of Washington, framed the chemical schedule, used the advice and aid of Dr. Grinnell Jones and Messrs. DeLong and Kirkpatrick, chemical experts of the Tariff Commission, and relied upon the survey of the chemical industry that the commission has worked upon intensively for the past three years.

"More than one hundred chemicals have been given specific enumeration for the first time in tariff history," explains Representative Longworth. "On the other hand, many other commodities, obsolete in commerce, have been carried in various tariff bills purely as a matter of custom, and these have been dropped altogether. Generally speaking, the rates of duty in the schedule are about the same upon the articles enumerated in the Payne law as in that law. The general rate of duty throughout the schedule has been established at a uniform level of about 25 per cent both ad valorem and specific. It is only in these particular products which represent new industries or materials essential to national preparedness that the rates are higher."

Comparison between the rates of the Fordney bill and the Republican Payne-Aldrich Act of 1909 and the Democratic Underwood-Simmons Act of 1913 is made difficult by the American valuation provisions of the Fordney bill. This provides that "the duties ad valorem shall be assessed upon the fair market value of the merchandise in the United States," and it results in the fact that a slight increase in the ad valorem rates will cause a substantial increase in protection.

Fertilizer materials, including ammonium sulfate and crude potash salts, become taxable for the first time in tariff history. Barytes and barium chemicals, magnesite, crude botanical drugs, synthetic camphor, and hydrogenated, vulcanized, and other chemically treated oils are recognized by the new tariff.

Another innovation of the Fordney bill is the power that is given the President, under circumstances warranted by the trade of the United States, to impose retaliatory duties or to adjust the rates along the principles of a bargaining tariff.

American surgical instruments and glassware are protected by the new tariff, and replying to charges that the proposed duties would bring hardships to college students, physicians, and hospitals, Representative Bacharach of New Jersey has declared that American products are the equal of Germany's and superior to Japan's.

On the floor of the House, opponents of the chemical and dyestuffs provisions of the bill introduced substitute amendments and attacked the chemical schedule. Representative Frear of Wisconsin was leader of the opposition. He also introduced a resolution requesting the Attorney General to bring legal proceedings to set aside the sale of 4000 alien chemical dye patents sold during the year 1919 by the Alien Property Custodian to the Chemical Foundation, Inc., and he made the charge that there is a dyestuffs lobby.

Tariff Commission Report on Dyes and Coal-Tar Chemicals in 1920

The report of the 1920 census of dyes and coal-tar chemicals by the Tariff Commission has just been issued. The output of dyes in 1920 was an increase of 40 per cent in both quantity and value over the preceding year, the report shows, and it is stated that "the value of the domestic output in 1920 was at least 120 per cent of the domestic consumption." The production for the first time of triphenyl phosphate in large quantities and of tricresyl phosphate in lesser amounts is an important development from a national standpoint, the report points out, as these two coal-tar products have been utilized as substitutes for camphor in the manufacture of pyroxylin plastics. As Japan has a monopoly on natural camphor, this is another step in chemical independence.

Alcohol Legislation

The prohibition legislation that has been threatening to affect the use of alcohol in the chemical industry has evolved another step. A third bill, H. R. 7294, has been drafted, and has been passed by the House, and is about to come up for action in the Senate. While the original provisions that alarmed chemists and the chemical industry and threatened to affect it seriously have been modified, the prohibition commissioner is still given the right to compel a change of formula of a medicine or perfume if he sees fit, and this is pointed out as dangerous to industry and autocratic in power.

Department of Commerce

Only one of the chiefs of the new industrial divisions of the Bureau of Foreign and Domestic Commerce of the Department of Commerce has been appointed as yet. W. S. Tower has been made head of the iron and steel industrial division. The chief of the chemical division that will be similarly established by Secretary Hoover to aid chemical industry in foreign trade has not yet been selected, although a decision is expected within the next few weeks.

Officials of the Department of Commerce, particularly the Bureau of the Census, are inviting coöperation of the chemical industry in working out plans for a monthly statistical service that will give data on stocks and production in the various chemical industries. W. M. Steuart, director of the Census, has sent circular letters to firms dealing in sulfuric acid, nitric acid, soda ash, and caustic soda, and asked their suggestions on forms and reports as a first step in the establishment of the service.

The Muscle Shoals Nitrate Plant

It seems that there is at last a possibility of the Muscle Shoals Nitrate Plant being placed into operation. Henry Ford has made a proposal for its utilization which Secretary of Commerce Hoover has forwarded to Secretary of War Weeks. The principal points in Mr. Ford's offer for the plant, on which the Government has spent $8,000,000 to date, are:

1—He will take a 100-year lease on the Wilson dam and No. 3 dam and electric installation when completed. This work is estimated to cost $28,000,000. After a short preliminary period, Mr Ford proposes to pay interest at the rate of 6 per cent on the sum of $28,000,000 and amortize not only this sum, but the entire cost of the two dams over a period of 100 years.

2—He will purchase all the nitrate plant and equipment, lands, steam plant, etc., for $5,000,000.

3—He will convert and operate the large nitrate plant (No. 2) for the production of fertilizer compounds and as a stand-by for government explosives in case of war and keep it up-to-date in both arts

4—He will limit the profits of the fertilizer plant to 8 per cent, an independent board embodying representatives of the American Farm Bureau Federation and the National Grange, and the Farmers' Union to certify this maximum.

It is understood that a number of tentative propositions made by the du Pont Powder Co., of Delaware, and a number of large chemical industries are also being considered by the government officials. Before any action can be taken on the offers or proposals, Congress will have to act.

The Fixed Nitrogen Research Laboratory

While Mr. Ford's offer makes it seem probable that the governmental nitrate plant will be placed into operation, an announcement of the transfer of the Fixed Nitrogen Research Laboratory, located at American University here, from the War Department to the Department of Agriculture, has assured the continuance of the investigative work on methods of fixing nitrogen from the air. Dr. R. C. Tolman, director, will remain in charge, and the entire personnel of 110 to 120, including 50 of the best trained experts in the world on nitrogen, is transferred. Most of the work of the laboratory has been done on the cyanamide process that is used in the Muscle Shoals plant, but the Haber and arc processes have also been studied. The laboratory will still consider nitrogen production from a military viewpoint, but it will do intensive work on problems of nitrogen supply for agricultural purposes. The laboratory and the Bureau of Plant Industry of the Department of Agriculture have in the past year made extensive field tests on various fertilizers produced at the Alabama plants, and it is planned to continue and enlarge these tests. Dr. R. O. E. Davis, in charge of the soil physical investigation of the Bureau of Soils, has been coöperating in these tests.

Budget for the Next Fiscal Year

The preparation of a budget for governmental expenditures during the next fiscal year is under way by the budget committee, headed by Gen. Dawes. Before the next two weeks have passed, it is expected that the budget will be presented to Congress. The scientific branches of the Government are joining in the trimming of estimates and the elimination of activities that can be dispensed with, and it may be that some lines of scientific work will be somewhat curtailed. But in the end it is believed that the general tightening up of the purse strings of the Federal treasury will react to the benefit of scientific work, and that the expenditure of more money for investigation and research will be possible as it is more fully realized that scientific research is the creative side of governmental expenditure.

National Research Council Bibliographies

The National Research Council has just begun the compilation of bibliographies of the different sciences. As in the tariff bill schedule, the first science of this program is chemistry. It is planned to list all published bibliographies on chemistry and as many unpublished or manuscript bibliographies as can be located. Dr. Clarence J. West is in charge of this work, and would appreciate any information on compilations of chemical works.

Work on heavy clay products will be conducted during this year by the Bureau of Mines with money that has been made available by Congress and contributions from the association of brick manufacturers.

The patent bill situation is just about as it was some weeks ago. The bill is still in the House, and there is a hopeful movement under way to bring it up for consideration again.

July 16, 1921

LONDON LETTER

By Stephen Miall, 28, Belsize Grove, Hampstead, N. W. 3, England

The coal strike has at last come to an end; it has been an interesting and costly experiment, not without some value. But if in some other country it is desired to repeat the experiment, all who have had actual experience of such a folly will advise friends to choose some more economical method of settling a difference of opinion. It would be far better to split the difference or spin a coin. So far as industry is concerned the last three months have been merely a blank, a gloomy interval between two periods of pretty bad trade. The dispute has been characterized by great patience and good humor on both sides; both owners and miners have watched their resources dwindling away, and our only satisfaction is that we know now that this country, and perhaps most other countries, can endure without a revolution, without rioting, without even ill temper, an industrial catastrophe of first-rate importance. In a few days coal will be coming from the pits, and by the end of July the mills which have for some months been in a state of suspended animation will again be busy. But it will take us a long while to recover from the loss of the last three months. Not only have the pits been idle, but chemical factories and indeed all other factories. With such an unprecedented period of inactivity and such an appalling loss of money, it is not a matter of surprise that for the last few months there have been in this country no items of news in the realm of industrial chemistry of any interest outside our borders.

What we have to consider here is not what new processes will be adopted but whether some of our largest enterprises can carry on during the next few years without reconstruction or drawing on reserves which have been accumulated as a precaution against a set of conditions which even the most cautious and pessimistic never expected would actually prevail.

The International Congress at Brussels

It was a refreshing change to get away from our own stagnation to attend the Congress of the International Union of Pure and Applied Chemistry at Brussels. The Belgian chemists were naturally present in force, and Messrs. Chavanne, Lucion, Swarts, Timmermans, and their colleagues arranged a very delightful and interesting reunion. On the question of an international committee to deal with atomic weights, the American delegates had naturally an important part to play, and I think Messrs. Conant, Cottrell, and Mackall can be congratulated on their efforts. The Americans have taken a leading part in the accurate determination of atomic weights and now that this branch of research seems likely to come to an end we fully expect their physical chemists to take an equally prominent position in some allied field of work. This International Union is now representative of practically the whole chemical world with the exception of Germany, and the international aspects of chemistry are considered and dealt with in as prompt and as satisfactory a manner as I believe to be possible.

Chemicals and Parliament

Measures to give some protection to the manufacture of dyestuffs and fine chemicals still afford debating points for the attention of a jaded House of Commons. But they excite comparatively little interest; such matters sink into insignificance by comparison with the great problems of the Irish question, the labor question, and the financial question.

A politician cannot be bothered with the methyl violet problem in the intervals of trying to clear up a mess which has ended in the Gilbertian position that Ulster which has for a century resisted Home Rule has now got it, and that the rest of Ireland which for the same period has agitated for it now refuses to consider it. A few years hence we shall offer Ireland a Republic and she will refuse the offer with scorn. Faced by such problems, how can the British government be expected to deal in a sensible manner with such trumpery matters as a flourishing chemical industry!

I imagine that even the manufacturers of dyestuffs themselves are more concerned in wondering whether the demand will ever become normal again, how long they can continue to work short time, and whether when the very bottom is reached they can win through without lightening their load by dropping a number of expensive items of plant and buildings left as a legacy by the great war.

The Labor Situation

A few days ago there was a very interesting debate in Parliament on the International Labor Conference held in Washington in November 1919. This conference started before the enthusiasm created by the war had come to an end and before we realized the great changes which bad trade and poverty would bring about. The French and Italians, the English and the Rumanians, all did their best to devise schemes which would be some improvement of the conditions of the great mass of population. Only the Americans, and to a less extent the Canadians, seemed skeptical. It now appears that they were right and that many of the hopeful projects of the other nations cannot be fully realized. The agreement come to about the eight-hour day seems to be unworkable in the exact shape in which it was adopted, and some other agreements will require considerable modification. Over here we are all hopeful of the work of the League of Nations and the International Labour Office, but we shall have to go slow if we are to improve industrial conditions without damaging industry by unwise interference.

July 11, 1921

PERSONAL NOTES

The degree of Doctor of Science has been conferred by Tufts College on **Frank William Durkee**, professor of chemistry at the college, and on **William Henry Nichols**, chairman of the Allied Chemical and Dye Corporation, New York City.

Dr. Harry F. Lewis, of the National Aniline and Chemical Co., Buffalo, N. Y., has been elected associate professor of chemistry at Cornell College, Mount Vernon, Iowa, where he will have charge of the work in theoretical and physical chemistry, and will assist **Dr. Nicholas Knight**, head of the department, with the other courses.

At the recent annual meeting of the American Institute of Fertilizer Chemists, the following officers were elected for the ensuing year: President, **Dr. Frank L. Parker**, of Charleston, S. C.; vice president, **A. G. Stillwell**, of New York City; treasurer, **W. J. Gascoyne, Jr.**, of Baltimore, Md.; secretary, **S. W. Wiley**, of Baltimore, Md.

Mr. Harry E. Wheeler, formerly with Massachusetts Gas Companies and affiliated companies, at Boston, Mass., has been appointed comptroller of the American Agricultural Chemical Co., with office in New York City.

Mr. Charles Copeland, assistant treasurer of E.I. du Pont de Nemours & Co., has been elected a member of the Board of Directors and secretary of the firm to fill the vacancies caused by the death of **Alexis I. du Pont**.

Dr. G. J. Fink, formerly with the Hooker Electrochemical Co., has been added to the technical staff of the chemical department of the National Lime Association, Washington, D. C.

Mr. C. S. Bryan, for several years connected with the Virginia-Carolina Chemical Co., as superintendent and research chemist, and more recently manager for the Charleston Chemical Co., Charleston, S. C., is now with the Provident Chemical Works of St. Louis, as chemical engineer.

By an order of the Secretary of Agriculture on July 30, **Mr. Walter G. Campbell**, assistant chief of the Bureau of Chemistry since 1916, was made acting chief to fill the place of Dr. Alsberg. **Dr. W. W. Skinner**, chief of the water and beverage laboratory since 1908, has been designated assistant chief.

Mr. C. J. West has left the position of director of the Information Department of Arthur D. Little, Inc., Cambridge, Mass., to become managing editor of the "Tables of Physical and Chemical Constants," which is being published by the National Research Council, in coöperation with the American Chemical Society. The work will have its headquarters at 1701 Massachusetts Ave., Washington, D. C.

Dr. Maurice L. Dolt is now research and plant chemist for the manufacture of food colors and pharmaceuticals with Calco Chemical Co., Bound Brook, N. J., having previously been research chemist with the American Cotton Oil Co., of Chicago, Ill.

Mr. J. C. Butcher, former owner of the Hood River Spray Co., and **Mr. W. B. Dickerson**, director of the Apple Growers Association, will launch a large spray factory at San José, Cal., at an early date. This factory will manufacture sprays of all kinds.

According to a recent announcement, **Mr. Bradley Stoughton** has resigned as secretary of the American Institute of Mining and Metallurgical Engineers, his resignation being accepted by the Institution.

Mr. Roy A. Weaver, upon completing his course in chemical engineering at Purdue University last spring, accepted a position in the chemical division of the Procter and Gamble Soap Co., Cincinnati, Ohio.

Dr. Howard Adler was recently appointed to an instructorship in the department of chemistry at the University of Chicago, Chicago, Ill.

Dr. H. Lee Ward, formerly of the National Aniline Co., has been appointed assistant professor of chemistry at Washington University, St. Louis, Mo., where he will have charge of the work in physical chemistry and applied electrochemistry.

Dr. J. W. Kimball, formerly research chemist at Delta Laboratory, E. I. du Pont de Nemours & Co., Arlington, N. J., has joined the staff of the National Aniline and Chemical Co., as research chemist at their works at Marcus Hook, Pa.

Mr. Sidney D. Kirkpatrick resigned as chemical expert for the U. S. Tariff Commission June 1 to become assistant editor of *Chemical and Metallurgical Engineering*, with headquarters in New York City.

Mr. Ralph Shriner has been appointed an instructor in chemistry at Washington University, St. Louis, Mo.

Mr. Walter G. Karr, formerly with the department of chemical research, Parke, Davis and Co., Detroit, Mich., is at present biochemist in charge of the chemical laboratories, Philadelphia General Hospital, Philadelphia, Pa.

Dr. Barnett Cohen, until recently engaged as research assistant in Public Health at Yale University, at present holds the position of associate chemist at the Hygienic Laboratory, U. S. Public Health Service, Washington, D. C.

Dr. F. A. Gilfillan recently received his Ph.D. from Yale, and has accepted a position on the research staff of the Calco Chemical Co., Bound Brook, N. J.

Mr. L. J. Bircher, formerly instructor in chemistry at Washington University, St. Louis, Mo., has accepted a position at Vanderbilt University, Nashville, Tenn.

Mr. O. D. Cunningham, previously with the National Aniline and Chemical Co., Buffalo, N. Y., where he carried on research in the physical chemistry department, is now associated in a similar capacity with the Republic Creosoting Co., Indianapolis, Ind.

Mr. C. A. Carlton, for the past two years secretary and chief chemist for the Avalon Rubber Manufacturing Co., Akron, Ohio, has joined the staff of the Duplex Tire and Rubber Co., Joplin, Mo., as secretary and factory manager.

Mr. William J. Husa, formerly research assistant in food chemistry with **Dr. H. C. Sherman**, at Columbia University, New York City, where he recently received his M.A. degree, will teach chemistry this coming year in the College of Pharmacy of the University of Iowa, Iowa City, Iowa.

Mr. George A. Olson has resigned as chemist of the Washington Agricultural Experiment Station and state chemist of the State of Washington, in order to accept the position as director of agricultural research and agricultural adviser for the Gypsum Industries Association, Chicago, Ill., which position was formerly held by **Dr. William Crocker**, plant physiologist of the University of Chicago. Through Dr. Crocker's assistance and direction several fellowships in various agricultural colleges were established.

Dr. Joseph L. Mayer, chief chemist of the research and analytical laboratories of the Louis K. Liggett Co., New York, has been appointed professor of analytical and pharmaceutical chemistry in the Brooklyn College of Pharmacy where he has been associate professor of analytical chemistry for several years.

Dr. J. H. Shrader, formerly with the U. S. Department of Agriculture, Washington, D. C., has been appointed director of the Bureau of Chemistry and Food, Health Department, Baltimore, Md.

Mr. E. J. Eimer has left the employ of the Hercules Powder Co., Parlin, N. J., and is now in partnership with **Mr. George Tierney** in the production of pyroxylin lacquers, under the firm name of the Paterson Chemical Co., Paterson, N. J.

Mr. Albert S. Richardson, research chemist at the Experiment Station of the du Pont Co., is at present director of research of Procter and Gamble Co., Ivorydale, Ohio.

Mr. S. M. Southard, who was connected with the Western Oil Refining Co., as purchasing agent, traffic manager, and chemical engineer, severed his connections with that firm to become affiliated with the Southern Oil Corp., Chicago, Ill. He was a short time ago appointed district manager in charge of the southwestern district with offices at Kansas City, Mo.

Mr. Max Y. Seaton, who was chemical engineer on the staff of the Dow Chemical Co., Midland, Mich., having particular charge of the oxychloride research division of that company, has taken over the direction of technical work for the National Kellastone Co., Chicago, Ill. He will also direct the technical work of the Sierra Magnesite Corporation, of Porterville, Cal.

Mr. C. Earl Littell, chemical engineer for the Providence Gas Co., Providence, R. I., has left that position to become assistant superintendent of the New Haven Gas Light Co., New Haven, Conn.

Mr. Philip B. Terry has resigned as development chemical engineer in the dye works branch at Jackson Laboratories, of E. I. du Pont de Nemours & Co., Deepwater Point, N. J., to enter the office of the Spaulding-Moss Co., Boston, Mass.

INDUSTRIAL NOTES

The War Department is to distribute more than 12,000,000 lbs. of picric acid to farmers for agricultural purposes. This surplus stock, accumulated for war purposes, is located at Sparta, Wis., and Wingate, N. M., and will be distributed through the Bureau of Public Roads of the Department of Agriculture, the only cost to farmers being freight charges and six cents a pound for placing the powder in the necessary cartridges.

Stanislaws C. Papp, inventor of an alleged process of making a substitute for gasoline from the fermented product of cornstalks and sugarcane, was sentenced on July 19, 1921, to from two and a half to five years in Sing Sing. Papp, who was also known as Professor F. John Chassler, was the head of the Fermogas Co., a million dollar stock company organized to develop the invention. During the war he succeeded in interesting the Government in his scheme, and army officers inspected his plant. It was alleged at the trial that cornstalk automotive liquid ran an engine only because alcohol had been added to the fermenting mass of cornstalks and water.

The plant of the Warner-Quinlan Asphalt Company at Linden, N. J., was seriously damaged by fire on July 19 and 20. The destruction involved eighteen asphalt tanks, thirty-three oil tanks, twelve gasoline tanks, sixteen stills, and practically all the buildings, including the administrative offices, the power house, the research laboratories, and the tool shop, as well as the dock at the water's edge, six tank cars, and half a mile of railroad track. There remain six or seven comparatively small gasoline tanks which were saved after they had already kindled, and two small brick buildings. The loss is estimated at $3,500,000.

The "Compagnie Nationale de Matières Colorantes" of Paris is to increase its capital from 1,000,000 to 79,000,000 fr. Attempts are now being made to standardize the names of dyes in France. The Union for the Development of the Dye Industry in France has with the assistance of the associated manufacturers issued its official register of dyes containing precise designations for about 260 dyes now placed upon the market.

Construction has been started on a sugar experiment station at Prague, Czechoslovakia, which is to be the most elaborate and up-to-date in Europe. Czechoslovakia is now producing 700,000 tons of sugar a year, and it is believed that 1,000,000 tons will soon be produced. The experiment station, which is a large factor in the plans for the development of the sugar industry, has been under consideration for several years.

The Home Grown Sugar Co., Ltd., of London, is to receive a second grant of £125,000 from the British government, provided it can itself raise £75,000. Last year the government allotted £250,000.

The plant of the Norvell Chemical Co., at Perth Amboy, N. J., was practically destroyed by fire on July 26. No estimate of the damage has been made.

The first conference of the complete Pharmacopeial Committee of Revision was held July 1 and 2, 1921, at Philadelphia, Pa. The first day was devoted to subcommittee conferences, and at the close of the day all subcommittees reported their current problems settled or decided as far as possible. The following day was devoted to a meeting of the General Committee. A committee was appointed to take up the recommendation of the Pharmacopeial Convention that a conference on international standards be called before the completion of the Tenth Revision of the U. S. P. An announcement was made of the authorization by the Board of Trustees of the use of the U. S. P. IX text for translation into Chinese. It is expected that this will be accepted by Chinese government officials and become the Pharmacopeia of China, First Edition. It was also announced that individual work on pharmacopeial problems could by special permission be released for publication. A conference was held with the Prohibition Commissioner in regard to the proposed coöperation between the Department and the Committee of Revision on all questions in which pharmacopeial alcoholic preparations are involved.

Messrs. M. R. Lamkey and Thomas F. Mains, plant physiologists of the State Agricultural Experiment Station, Newark, Del., after an inspection of property at South Wilmington held to have been damaged by fumes from the plant of the Pyrites Co., Ltd., have formally reported to the City Council of Wilmington that there is no absolute evidence that the damage was done by fumes or smoke from this plant, and that it was probably due to severe frosts in the early spring. Referring to the delay of a month before the investigation, because of failure to call on the station chemists, the report states that many natural conditions can produce injuries so nearly similar to fumes or smoke injury that no investigation can distinguish the two after an exposure of several days to weather conditions; that the injuries must be seen as they are produced, and the conditions under which they are produced must be known before a conclusive statement can be made.

The American Zeolite Co., of Paterson, N. J., manufacturers of a chemical extensively used by silk dyeing concerns for the softening of water, has procured from Chancery Court an order restraining its former chemist and superintendent, Oswin W. Wilcox, from divulging the secret process by which the product is manufactured. The company alleged that Wilcox, in spite of having signed a contract not to reveal the process in question, had entered into negotiations with other concerns with the view of manufacturing a similar product through the use of the American Zeolite Company's secret process.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

NATIONAL ACADEMY OF SCIENCES

Memoirs of National Academy of Sciences. 1920. Volume 16, 3rd memoir, 418 pp. Paper, 65 cents. **Part V. Recalculation of Atomic Weights with Bibliography.** F. W. Clarke. 4th edition, revised and enlarged.

TARIFF COMMISSION

Tariff Information Surveys. Revised edition. 1921. (First edition was issued by Ways and Means Committee.)

B-2. On articles in Paragraphs 73 and 74 of tariff act of 1913 and related articles in other paragraphs. **Lime, gypsum, and cements.** 51 pp. Paper, 5c.

B-3. On articles in Paragraph 75 of tariff act of 1913 and related articles in other paragraphs. **Abrasive materials.** 46 pp. Paper, 5c.

B-4. On articles in Paragraph 76 of tariff act of 1913 and related articles in other paragraphs. **Clays and earths.** 63 pp. Paper, 5c.

B-7. On articles in Paragraph 81 of tariff act of 1913 and related articles in other paragraphs. **Manufactured earthy and mineral substances.** 5 pp. Paper, 5c.

B-8. On articles in Paragraphs 81 and 82 of tariff act of 1913 and related articles in other paragraphs. **Carbon products.** 30 pp. Paper, 5c.

C-1. On articles in Paragraph 102 of tariff act of 1913 and related articles in other paragraphs. **Ferroalloy industries.** 160 pp. Paper, 15c.

FL-1. On articles in Paragraph 387 of tariff act of 1913 and related articles in other paragraphs. **Acids exempt from duty.** 38 pp. Paper, 5c.

FL-2. On articles in Paragraphs 388–390 of tariff act of 1913 and related articles in other paragraphs. **Drugs exempt from duty.** 94 pp. Paper, 10c.

FL-5. On articles in Paragraphs 399–402 of tariff act of 1913 and related articles in other paragraphs. **Fertilizer, raw materials exempt from duty.** 42 pp. Paper, 5c.

FL-7. On articles in Paragraphs 409–417 of tariff act of 1913 and related articles in other paragraphs, **Petroleum oils, asphalt and bitumen, waxes, vegetable and mineral.** 37 pp Paper, 5c.

FL-8. On articles in Paragraphs 418–428 of tariff act of 1913 and related articles in other paragraphs. **Bismuth, etc.** 34 pp. Paper, 5c.

FL-17. On articles in Paragraph 500 of tariff act of 1913 and related articles in other paragraphs. **Copals, shellac, and other varnish gums,** naval stores industry, gutta-percha and india rubber. 63 pp. Paper, 5c.

G-33. On articles in Paragraph 234 of tariff act of 1913 and related articles in other paragraphs. Starch and related materials. 36 pp. Paper, 5c.

PUBLIC HEALTH SERVICE

Fractionation of Chaulmoogra Oil. A. L. DEAN AND RICHARD WRENSHALL. Reprint No. 646 from Public Health Reports. 20 pp. Paper, 5 cents. 1921.

Preliminary Note on a Stable Silver Vitamine Compound Obtained from Brewers' Yeast. ATHERTON SEIDELL. Reprint No. 648 from Public Health Reports. 7 pp. Paper, 5 cents. 1921.

The Comparative Toxicity of Thymol and Carvacrol (Isothymol). A. E. LIVINGSTON. Public Health Reports, **36,** 1317–31. The conclusions reached are: (1) The toxicity of thymol and of carvacrol on rabbits is essentially the same; (2) the toxicity of thymol and of carvacrol as tested on paramecia shows no striking difference; and (3) tests on earthworms indicate that the relative anthelmintic value of thymol and carvacrol is practically the same.

GEOLOGICAL SURVEY

The Iron-Ore Resources of Europe. MAX ROESLER. Bulletin 706. 152 pp. This bulletin gives a summary of the facts concerning the deposits of iron ore in Europe and estimates of the quantities of ore and of iron they contain. It reports no original research work; it is simply the result of a study of the work of many writers and is an attempt to reduce the variant products of that work to common values.

Antimony in 1919. F. C. SCHRADER. Separate from Mineral Resources of the United States, 1919, Part I. 25 pp. Published June 6, 1921. As there was no domestic production in 1919, the reader is referred to the report for 1918 for the latest descriptive statement on that phase of the subject. During the year the Government's large war surplus stock was absorbed, and at the end of the year the stock left throughout the country was low. Stocks in bonded warehouses amounted to about half of what they were at the beginning of the year. As there seems to be a surplus of antimony ores for the entire world, there is no reason to expect that prices of antimony will increase during 1921 unless there should be a greatly increased tariff placed upon antimony and antimony ores, or new uses of considerable extent for antimony should be found.

Mineral Resources of the United States in 1920. Preliminary Summary. Introduction by G. F. LOUGHLIN. statistics assembled by MARTHA B. CLARK from data furnished by specialists of the Division of Mineral Resources. 123 pp. Published July 7, 1921. The year 1920 showed, on the whole, an improvement over 1919 in the quantity and value of mineral products sold and made a new record in the total value of mineral products ($6,707,000,000), but the conditions of operation remained unfavorable and the marked increase in value was not so much a result of renewed prosperity as of increased costs of operation. The two years presented a contrast in that 1919 began in a period of depression that closely followed the signing of the armistice and continued until autumn, whereas 1920 began in a period of renewed demand, except for metals, which also lasted until autumn, when a period of general stagnation began that has continued until the present time (June 1921).

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, March 1921. W. W. ADAMS. 11 pp. Paper, 5 cents. 1921.

BUREAU OF STANDARDS

Analyzed Iron and Manganese Ores—Methods of Analysis. Circular 26, 4th ed. 20 pp. Paper, 5 cents. 1921.

Nickel. Circular 100. 106 pp. Paper, 20 cents. 1921. The circular is divided into three parts; A, nickel; B, alloys of nickel; and C, appendices. The Bureau of Standards is continually in receipt of requests for information concerning the properties, statistics, and manufacture of metals and alloys, and it is to meet such requests relative to nickel that this circular was issued.

Thermal Expansion of Copper and Some of Its Important Industrial Alloys. PETER HIDNERT. Scientific Paper 410. 159 pp. Paper, 25 cents. Data on the thermal expansion of 128 samples of copper and its important alloys of various compositions, heat treatments, mechanical treatments, etc., are presented. Practically all available information on the thermal expansion of copper and its alloys is briefly reviewed. A description of the apparatus and the preparation of the samples, etc., are given.

Test of Centrifugally Cast Steel. Technologic Paper 192. Paper, 10 cents. Opportunity was given to the Bureau of Standards to examine in detail the physical and chemical characteristics of six centrifugal castings made by the Millspaugh process. The results are interesting as showing what may be expected from such metal as compared with the product of the more familiar manufacturing processes. This investigation shows that highly satisfactory castings which are physically sound and free from serious segregation may be produced by the centrifugal method. It is shown that the properties of these castings can be improved greatly by subsequent heat treatment, such that the metal may be put in a condition to compare favorably with metal that has been forged.

DEPARTMENT OF AGRICULTURE

Commercial Utilization of Grape Pomace and Stems from the Grape-Juice Industry. FRANK RABAK AND J. H. SHRADER. Department Bulletin 952. 24 pp. Paper, 10 cents. Issued June 4, 1921. The investigation shows that the waste which accumulates annually in large quantities at the various grape-juice plants can be made to yield a number of commercially valuable products. Attention is called to the proper and most economical methods for handling the waste.

Care of Leather. F. P. VEITCH, H. P. HOLMAN, AND R. W. FREY. Farmers' Bulletin 1183. 18 pp. Reprinted 1921. Paper, 5 cents.

Freezing Injury to Potatoes When Undercooled. R. C. WRIGHT AND G. F. TAYLOR. Department Bulletin 916. 15 pp. Paper, 5 cents. Issued June 13, 1921. This bulletin gives the results of a portion of the work carried on under the project "Factors Affecting the Storage Life of Vegetables."

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Standard Specifications and Tests for Portland Cement. Text as adopted by the American Society for Testing Materials and by the United States Government. French-English edition, prepared under the supervision of the Bureau of Standards. Industrial Standards No. 101. Revised 1921. 46 pp. Paper, 10 cents. These specifications are the result of several years' work of a special committee representing a United States government departmental committee, the board of direction of the American Society of Civil Engineers, and Committee C–1 on cement of the American Society for Testing Materials, in coöperation with Committee C–1.

Standard Specifications for Turpentine. Text as adopted by the American Society for Testing Materials. Adopted, 1915. French-English edition, prepared under the supervision of the Bureau of Standards. English text copyrighted in the United States by the American Society for Testing Materials. The French text is not copyrighted. Industrial Standards No. 161. 10 pp. Paper, 5 cents. 1921. These specifications apply both to the turpentine that is distilled from pine oleoresins, and commonly known as "gum turpentine" or "spirits turpentine," and to the turpentine commonly known as "wood turpentine" that is obtained from resinous wood, whether by extraction with volatile solvents, or by steam, or by destructive distillation.

COMMERCE REPORTS—JUNE 1921

The production of leucite, from which a **potash fertilizer** is derived, is reported in Italy. Leucite is now used extensively in Italian agriculture where formerly German potash was used. (P. 1239)

The production of **petroleum** and petroleum products in Germany is reviewed. (Pp. 1284–5)

Investigations are being conducted with a view to utilizing Australian timber in the manufacture of **wood pulp.** (P. 1286)

The discovery of **bauxite** in British territories has aroused so much interest in the research work that Parliament is being asked to devote the sum of £100,000 for overseas research work. (P. 1295)

The Imperial Mineral Resources Bureau has printed as a part of its annual volume on the Mineral Resources of the British Empire and Foreign Countries, a valuable report on the production and consumption of **zinc.** The chief zinc-bearing minerals, the probable need of using complex ores in future, the production in various countries, plant extension during the war, and the smelter output from 1913 to 1919 are described, among other things. (Pp. 1318–20)

The Spanish committee to supervise the exportation of flaxseed, linseed oil and cakes, peanuts, and other **oil-bearing seeds,** created by Royal Order of September 13, 1918, has been abolished. (Pp. 1329–30)

The Japanese navy is reported to be in need of **oil.** (P. 1344)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil material by Turkey during the years ending March 13, 1912, 1913, and 1914, and summary figures for the period of September 1916 to August 1917, inclusive. (P. 1348)

Some deposits of **kaolin** have been discovered in Puolanka and neighboring parishes of Osterbotten, Finland, which are considered of great economic importance. (P. 1374)

The following table gives the world's production (in long tons) of **chromite ore** for 1914–1919. Except where otherwise stated, the statistics are from official sources. (P. 1382)

COUNTRIES	1914	1915	1916	1917	1918	1919
United Kingdom	99	....	....	....	....	....
India	5,888	3,768	20,159	27,061	57,773	31,594
New Caledonia[1]	41,325	56,550[2]	72,924[2]	41,218[2]	26,000	....
Southern Rhodesia	43,042	54,090	79,349	65,146	27,936	31,501
Canada	121	11,019	24,568	32,790	19,637	7,443
Australia	648	757	451	1,343	718	246
Bosnia	207	....	....	.	....	....
Greece	6,946	10,252	9,721	6,642	10,715	....
Japan	2,049	2,895	8,147	8,800	7,128	....
United States	591	3,280	47,034	43,725	82,355	3,900
Total of items given	100,916	142,611	262,353	226,725	232,262	74,594

[1] Mineral industry.
[2] Statistics of Iron and Steel and Allied Trades Federation.

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil materials by British North Borneo, Territory of Sarawak, and State of Brunei, during the years 1915, 1916, and 1917. (P. 1407)

The attention of Chile is being focused on various projects aiming toward the revival of **nitrate** sales. (P. 1426)

The Java **rubber** situation is reviewed. (Pp. 1432–3)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil materials by British Oceanica, other than Australia and New Zealand, during the years 1917, 1918, and 1919. (Pp. 1436–7)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil material by the British possessions in the Mediterranean for the three latest years for which figures are available. (P. 1440)

A decrease in the Mexican **oil** exports is shown for the month of April. (P. 1441)

Finland's **cellulose** market is still uncertain. (P. 1445)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil material by the British West Indies. (P. 1454)

The government of India has recently issued a "Report on **Lac** and **Shellac**" as a part of "Indian Forest Records," which it is believed will be very serviceable and of interest to users of shellac. (P. 1465)

The European markets, including Danzig, England, France, Greece, Ireland, and Rumania, for **paints** and **varnishes,** are reviewed. (Pp. 1466–79)

The Italian government will prohibit the importation of **synthetic dyes** and **intermediates** except under special license. This prohibition became effective on June 3, 1921. (P. 1489)

The **base metal** industry of Australia is passing through the most critical period in its history, with costs of production out of all proportion to market prices, in consequence of which many mining companies have been compelled to suspend operations. (P. 1496)

The Imperial Mineral Resources Bureau has issued a report on **aluminium** and **bauxite,** which contains the following tables showing seven years' output of aluminium and bauxite (in tons):

COUNTRIES	1913	1914	1915	1916	1917	1918	1919
				BAUXITE			
United Kingdom	6,055	8,286	11,723	10,329	14,724	9,589	9,221
British Guiana	....	....	....	....	2,037	4,199	....
India	1,184	514	876	750	1,363	1,192	1,682
France	304,323	....	55,614	104,493	118,973	....	160,820
Hungary	....	....	58,118	....	....	....	....
Italy	6,840	3,843	5,805	8,744	7,664	7,675	2,924
Spain	....	....	....	....	....	453	1,751
United States	210,241	219,318	297,041	425,100	568,690	605,721	376,566
TOTAL	528,643	231,961	429,177	549,416	713,451	628,829	552,964
				ALUMINIUM			
United Kingdom	7,500	7,400	7,000	7,600	7,000	8,200	8,000
Canada	6,000	6,500	6,000	7,500	8,000	8,000	8,000
Austria	2,000	2,000	....	....	....	....	....
France[1]	13,283	9,803	5,920	9,447	10,886	11,826	12,000
Germany	1,000	1,000	1,000	8,000	20,000	25,000	12,000
Italy[1]	860	922	889	1,108	1,712	1,687	2,000
Norway	2,000	4,000	8,000	12,000	15,000	15,000	10,000
Switzerland	10,000	15,000	10,000	12,500	15,000	15,000	15,000
United States	29,000	41,500	44,500	62,500	80,000	85,000	80,000
TOTAL	71,643	88,125	83,309	120,655	157,598	169,713	147,000

[1] Official figures; 1919 figure estimated.

(P. 1449)

The following data are given concerning **oil products** shipped from Polish refineries during 1920, these being in addition to 3740 carloads of crude oil which were exported:

PRODUCTS	Domestic Consumption Cubic meters	Exports Cubic meters	Total Cubic meters
Gasoline	502,776	223,589	726,365
Kerosene	867,773	577,098	1,444,871
Gas oil	200,035	368,017	568,052
Lubricants	454,232	356,425	810,657
Paraffin	87,497	92,939	180,436
Other products	466,626	378,042	844,668
TOTAL	2,578,939	1,996,110	4,575,049

Other interesting notes on the Polish oil industry are cited. (Pp. 1509–10)

The Bolivian duty on **stearin, paraffin, chemicals,** and **drugs** has been revised. (P. 1521)

European markets for **paints** and **varnishes,** including Bulgaria, Finland, Italy, Scotland, Spain, Switzerland, and Wales, are reviewed. (Pp. 1525–35)

The use of **alcohol** as locomotive fuel is reported in Brazil. (P. 1535)

The production of **alcohol** in Poland this year will be about 40,000,000 liters, of which 30,000,000 liters will be exportable. Last year's alcohol production was only 10,000,000 liters. (P. 1537)

Provisions of the new Bolivian **mineral oil** concession law are cited. (Pp. 1537–8)

It is stated that the **silver** deposits in the Philippine Islands can be worked advantageously on a commercial basis. (P. 1538)

The locations in which **graphite** may be found in the Far East are described, as well as the product found. (P. 1547)

Investigations are being made into the medicinal properties of a forest tree indigenous to parts of Bihar and Bengal. The experiments thus far conducted raise the hope that the drug made from the infusion of the leaves may be used as an **antifebrile.** (P. 1551)

The **edible oil** and **bean cake** industry in Japan is reviewed. (Pp. 1558–9)

The **natural resources** of the Isthmus of Karelia are described. (Pp. 1562–3)

Raw materials are now available in Burma, and the prospects are that she may become self-supplying so far as **soap** is concerned. (P. 1571)

The twenty-nine active distilleries of **industrial alcohol** now in operation in Buenos Aires depend entirely upon domestic products for their raw materials. (P. 1573)

Statistics are given showing the imports and exports of **vegetable oils** and vegetable-oil material by Chile during the years 1916, 1917, and 1918. (P. 1583)

There is a considerable opportunity for the sale in Aleppo, Syria, of various **metals,** such as copper, zinc, pewter, tin plate, silver, lead, aluminium, etc., all of which are produced in abundance in the United States. (P. 1596)

The price of **copper** is beyond any control in Australia, and there appears to be no hope of meeting the present financial loss without a reduction of wages and a rearrangement of working hours. (P. 1608)

Recent exploration and development have revealed enormous deposits of **osmiridium** and **gold-bearing gravels** in the valleys of the large rivers of the western division of Tasmania. (P. 1609)

Sulfate of ammonia continues to be one of the most important products of the Scottish mineral oil industry. (P. 1625)

Olive oil production in Spain in 1920 decreased from 3,363,937 metric quintals in 1919 to 3,169,637 metric quintals. (P. 1660)

A new method of extracting **aluminium** from a certain mineral is the result of the investigations which have been carried out by the Japanese experiment station. A great refinery plant driven by electric power will be established at Yoyogi. A project is under contemplation to establish a semigovernmental company for the manufacture of aluminium by the new method, which will enable the production of aluminium of more than 99 per cent. (P. 1664)

Far Eastern markets for **paints** and **varnishes,** including Hongkong, India, Japan, Manchuria, New Zealand, and Siam, are described. (Pp. 1670–79)

Community buying of **fertilizer,** begun in Spain in 1911 and discontinued during the war, has been reëstablished. (Pp. 1684–5)

Cuban imports of **chemicals, gums, etc.,** are reviewed. (Pp. 1694–5)

The manufacture of **industrial alcohol** is being encouraged by the Guatemalan government. (P. 1696)

The manufacture of "Penrol," a **gasoline substitute,** on a large scale is contemplated in South Africa. It will be produced from maize or mealies (corn) grown locally. (P. 1708)

The following table gives the total exports of mechanical wood **pulp** (in tons) from Christiania and the whole of Norway during the past three years:

YEAR	All of Norway		Christiania	
	Dry	Wet	Dry	Wet
1920	9,647	376,323	4,372	32,997
1919	19,925	355,458	7,463	44,984
1918	42,002	268,994	12,522	42,176

(P. 1727)

There is an abundant supply of raw materials in the Philippine Islands for the manufacture of **industrial alcohol.** (P. 1729)

The utilization of the **oil** from **rubber seeds** produced on rubber plantations in the Dutch East Indies now seems probable (P. 1744)

There was a total production of 502,931 metric tons of **phosphate** in Algeria during 1920. (P. 1792)

The Argentine **whale** and **seal oil** industry is reviewed. (P.1814)

A plant has been established near Turin for the transformation of explosives into **nitrates** for agricultural uses. (P. 1831)

The Leeds power stations are employing **oil fuel** with great success and with a big reduction in the consumption of coal. (Pp. 1846–8)

BOOK REVIEWS

Chronology of Iron and Steel. Compiled by S. L. GOODALE, Professor of Metallurgy, in the University of Pittsburgh, and edited by J. R. SPEER. 294 pages. $6^3/_4$ in. x 4 in. Handbook style, bound in imitation leather. Published by the Pittsburgh Iron and Steel Foundries Co., of whose Board the editor of the book is chairman. 1920. Price, $5.00.

The editor in the foreword points out how almost everything that is made by man which surrounds us in daily life is related to man's ability to smelt iron. A brief etymological statement about the words "iron" and "steel" is given, followed by the chronology grouped in thirteen arbitrarily chosen periods.

The arrangement of the subject matter is strictly chronological. The style is that of direct affirmative statement. The entries of chronological events number roughly close to 2000 and constitute a wonderful and delighting fund of information.

The context seems to the reviewer to be substantially correct. However, it is regrettable that neither authorities nor sources of information are cited. Neither is any intimation given as to the method of choosing as to points of chronology and identity of pioneer, about which doubt exists. An index including specific reference to each subject entered in the text, even though some subjects would have a good many page-listings, would add greatly to the accessibility of the subject matter. The index reference would be far more convenient if by pages instead of years, as now.

Some items whose connection with the chronology of iron and steel is not indicated are introduced. For example: The first act (in 1789) in building up of our present tariff system; also the founding of Rensselaer Polytechnic Institute in 1824; the first American Edition of the Bible in 1743. But these rather add to the interest of the book.

The book represents a large amount of painstaking labor in its compilation, and is a contribution which in a future edition, with authorities cited and a better index, can come to be a reference key of real value in its field. GEORGE M. BERRY

Technical Methods of Analysis. Methods employed in the Laboratories of Arthur D. Little, Inc. Edited by ROGER CASTLE GRIFFIN. xv + 666 pages. McGraw-Hill Book Co., New York, 1921. Price, $6.00.

This book is not a treatise on analytical chemistry. It is an attempt to describe in concise form the methods of assay which have been found useful in industry. Needless to say, no single book can completely cover this field. The most that can be expected in any such book is a selection of the most important methods of test in each industrial field, and a bibliography which will bring to the attention of the analyst or assayer the references to other methods. The usefulness of such a work is primarily to the general analytical chemist and assayer, for it cannot be expected that a general work of this type can supplant the many books on technical analysis available to the works chemist in his own field of industry; but to the analytical chemist in general practice, who is called upon to examine or to assay the products of a great variety of industries, such a work as this supplies a permanent want. The great variety of industries with which the methods of analysis described in this volume have to do makes it reasonably certain that almost all general analysts or assayers will find the book valuable. In some lines of industry the testing of the materials used and produced is better known than in others, and in this book more attention seems to have been given to the materials with which the general analyst is less familiar and in which the analytical methods used are more difficult to discover.

Only a few typographical errors are noticed, though a conspicuous one is on page 572, where tri-calcium silicate and di-calcium aluminate are described as "dry calcium silicate" and "dry calcium aluminate." PARKER C. MCILHINEY

Les Vernis. By CH. COFFIGNIER. viii + 640 pp. 37 illustrations. (Vol. XL of Encyclopédie de Chimie Industrielle, edited by M. Matignon.) J. B. Baillière et Fils, Paris, 1921.

Prepared as a reference volume in an encyclopedic series, this book has as its outstanding feature a comprehensive descriptive list of the raw materials of varnish making, occupying more than half its pages. Of especial value is the description of the resins, giving data on solubility in various solvents, density, melting point, etc., with brief references to commercial characteristics and analytical tests. A catalog of "varnish gums" modern enough to be worth referring to has heretofore been a serious lack.

The remainder of the book, which describes the processes of varnish making, differentiates the products in a general way and lists a number of formulas of all kinds, is of much less value. The section devoted to technique refers to the processes developed by the author in collaboration with others for rendering varnish resins soluble by means of naphthalene and copal oil without previous fusion, and for the production of ester resins; but in other respects is far from up-to-date. The reference to the technique of China wood oil varnishes is much too brief. Many of the formulas presented in the collection in the latter part of the book are worthless, being either obsolete, too vague to be reproduced, or impossible, as the author himself states in giving them; they are apparently presented merely as curiosities. The impression of the status of the varnish industry in France gained by the reader is that it is in a rather backward condition, working with small quantities and primitive apparatus.

The methods of analysis described in connection with the section on raw materials are fairly complete, but those for finished products are rudimentary. The method of analysis for oil varnishes proposed by Parker C. McIlhiney (the Saints have mercy on the murdered spelling of his name!), which probably represents the most advanced work that has been published on this subject, is given, but is dismissed as impractical.

The author gives the impression of knowing more than he is willing to write—too often the case with publications in this field. CHARLES R. BRAGDON

NEW PUBLICATIONS

Biological Chemistry: Practical Biological Chemistry. G. Bertrand and P. Thomas. Translated from the 3rd edition by Hector A. Colwell. 380 pp. 61 illus. Price, $3.75. D. Van Nostrand Co., New York.

Chemistry for Public Health Students. E. Gabriel Jones. 253 pp. Price, $2.50. D. Van Nostrand Co., New York.

Chemists' Year Book. 1921. Edited by F. W. Atack and L. Whinyates. Vols. I and II. 1142 pp. Price, 7s. net. Sherratt and Hughes, Manchester, England.

Dairy Bacteriology. Orla-Jensen. Translated from 2nd Danish edition with additions and revisions by P. S. Arup. 180 pp. 70 illus. Price, $3.00 net. P. Blakiston's Son and Co., Philadelphia.

Dye Chemistry: The Fundamental Processes of Dye Chemistry. Hans Edward Fierz-David. Translated by Frederick A. Mason. 240 pp. J. and A. Churchill, London.

Elements of Engineering Geology. H. Ries and Thomas L. Watson. 365 pp. Price, $3.75 net. John Wiley and Sons, Inc., New York.

Flotation: Die Schwimmaufbereitung der Erze. Paul Vageler. 98 pp. Illustrated. Price, 80 cents. Theodor Steinkopff, Dresden, Germany.

Foundations of Chemical Theory. The Elements of Physical and General Chemistry. R. M. Caven. 274 pp. 46 illus. Price, $4.00. D. Van Nostrand Co., New York.

General Chemistry: Chimica Generale. Giuseppe Bruni. 240 pp. Illustrated. Price, L.25. Libreria Editrice Politecnica, Milan, Italy.

Handbook of Engineering Mathematics. Walter E. Wynne and William Sparagen. 2nd edition, revised and enlarged. 285 pp. Illustrated. Price, $2.50. D. Van Nostrand Co., New York.

Inorganic Chemistry: Textbook of Inorganic Chemistry for Colleges. James F. Norris. International Chemical Series. 677 pp. 43 illus. Price, $3.50. McGraw-Hill Book Co., Inc., New York.

Manufacture of Earth Colors. Josef Bersch. Translated from the 3rd German edition by Charles Salter. 216 pp. 31 illus. Price, $3.00. D. Van Nostrand Co., New York.

Organic Chemistry: A Textbook of Organic Chemistry. Joseph Scudder Chamberlain. 959 pp. Price, $4.00 net. P. Blakiston's Son and Co., Philadelphia.

Organic Compounds of Mercury. Frank C. Whitmore. American Chemical Society Monograph Series. 397 pp. Price, $4.50. Chemical Catalog Co., Inc., New York.

Physical Chemistry for Colleges. E. B. Millard. International Chemical Series. 416 pp. Price, $3.50. McGraw-Hill Book Co., Inc., New York.

Qualitative Analysis: A Course of Qualitative Chemical Analysis of Inorganic Substances. Olin Freeman Tower. 4th edition, revised. 89 pp. Price, $1.50 net. P. Blakiston's Son and Co., Philadelphia.

Steel: Heat Treatment of Soft and Medium Steels. Federico Giolitti. Translated by E. E. Thum and D. G. Vernaci. 374 pp. 214 illus. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Tables of Refractive Indices. Vol. II—Oils, Fats and Waxes R. Kanthack. Edited by J. N. Goldsmith. 295 pp. Price, £1 5s. net Adam Hilger, Ltd., London.

Vegetable Histology: Elements of Vegetable Histology. C. W. Ballard. 260 pp. 75 illus. Price, $3.00. D. Van Nostrand Co., New York.

Volumetric Analysis. Charles H. Hampshire. 3rd edition. 120 pp. Price, 7s. 6d. net. J. and A. Churchill, London.

Waste: Collection and Disposal of Municipal Refuse. Rudolph Hering and Samuel A. Greeley. 653 pp. 131 illus. Price, $7.00. McGraw-Hill Book Co., Inc., New York.

Wood Products. Distillates and Extracts. Part I—The Chemical Products of Wood Distillation. Part II—Dyeing and Tanning Extracts from Wood. P. Dumesny and J. Noyer. 3rd edition, revised and enlarged. 360 pp. 118 illus. Price, 22s. Scott, Greenwood and Son, London.

RECENT JOURNAL ARTICLES

Aldehyde Content of Sulfite Alcohol. Rudolf Sieber. *Pulp and Paper Magazine of Canada*, Vol. 19 (1921), No. 27, pp. 719, 728. Translated from *Svensk Pappers-Tidning.*

Ammonia Synthesis: Ancora sulla Sintesi dell' Ammoniaca. L. Cambi. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 5, pp. 199–202.

Calculating Boiler Heat Balances. H. D. Fisher. *Combustion*, Vol. 5 (1921), No. 1, pp. 18–24.

Catalysis: Les Principales Applications de la Catalyse. P. Razous. *L'Industrie Chimique*, Vol. 8 (1921), No. 89, pp. 213–16.

Cellulose: Determination of Alpha-, Beta-, and Gamma-Cellulose. *Paper*, Vol. 18 (1921), No. 14, pp. 19, 25. Translated from *Die Chemische Untersuchung Pflanzlicher Rohstoffe und der daraus Abgeschiedenen Zellstoffe.*

Cellulose: Oxy- und Hydrocellulose. Hans Pringsheim *Cellulosechemie* (supplement to *Der Papier-fabrikant*), Vol. 2 (1921), No. 5, pp. 57–61.

Coal: Power Plant Coal and Its Selection. Robert June. *The Gas Age*, Vol. 47 (1921), No. 12, pp. 514–17.

Color Classification of Blast Furnace Slags. Wallace G. Imhoff. *Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 7 pp. 433–34.

Drop Forging: Billets for the Drop Forger. Harry Brearley. *Forging and Heat Treating*, Vol. 7 (1921), No. 6, pp. 307–13.

Dye House Cost Variations. H. D. Martin. *Textile Colorist*, Vol. 43 (1921), No. 511, pp. 454–55.

Dyeing: Continuous Dyeing of Cotton Goods. Morris M. Rivelis. *Textile World*, Vol. 59 (1921), No. 26, pp. 35–37.

Fireclay: The Reversible Thermal Expansion of Fireclay and Other Refractory Materials. H. S. Houldsworth and John W. Cobb. *Journal of the Society of Glass Technology*, Vol. 5 (1921), No. 17, pp. 16–44.

Flash Point Apparatus. F. Wilbur Shulenberger. *Paint, Oil and Chemical Review*, Vol. 71 (1921), No 24, pp. 9, 18–20.

Flue Dust Production and Consumption. F. H. Willcox. *Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 7, pp. 420–21.

Gas: The Application of Gas to Japanning. W. J. Hampton. *The Metal Industry*, Vol. 19 (1921), No. 7, pp. 278–79.

Gas By-products as Raw Material. R. S. McBride. *The Gas Age*, Vol. 47 (1921), No. 11, pp. 455–59.

Glass: The Development of Various Types of Glass. A Comparison of the Alkali-Lime-Silica and the Alkali-Lead Oxide-Silica Glasses. C. J. Peddle. *Journal of the Society of Glass Technology*, Vol. 5 (1921), No. 17, pp. 72–106.

Glass: Some Calculations of Glass Technology. J. B. Krak. *The Glass Industry*, Vol. 2 (1921), No. 7, pp. 159–60.

Glass: The Thermal Expansion and Annealing Temperature of Glass. W. B. Pietenpol. *The Glass Industry*, Vol. 2 (1921), No. 7, pp. 162–65.

Guanidine: The Preparation of Guanidine Salts and of Nitroguanidine. Thomas Ewan and John H. Young. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 11, pp. 109*t*–112*t*.

Illipe Butter: Detection and Estimation of Illipe Butter Used as Substitute for Cacao Butter. Francis G. H. Tate and John W. Pooley. *The Analyst*, Vol. 46 (1921), No. 543, pp. 229–37.

Indicators: Sur l'Emploi des Indicateurs Colores en Acidimetrie et en Alcalimetrie. V. Auger. *Bulletin de la Société Chimique de France*, Vol. 29 (1921), No. 6, pp. 229–351

Leather: On Certain Characteristics of Fresh Steer Hide. George D. McLaughlin. *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 6, pp. 295–309.

Leather: The Determination of Alkaline Sulfides in Lime Liquors. Fini G. A. Enna. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 5, pp. 131–37.

Lithopone, Its History and Manufacture. John S. Williams, Jr. *The Rubber Age*, Vol. 9 (1921), No. 5, pp. 167–68.

Milk: Chemistry of Milk Curd Modification in Infant Feeding. Robert Wood Terry. *Journal of the American Pharmaceutical Association*, Vol. 10 (1921), No. 5, pp. 345–62.

Nickel: The Latent Heats of Fusion of Nickel and Monel Metal. Walter P. White. *Chemical and Metallurgical Engineering*, Vol. 25 (1921), No. 1, pp. 17–21.

Oil: The Carbonization of Lubricating Oils in Internal-Combustion Engines. Frederic H. Garner. *Journal of the Institution of Petroleum Technologists*, Vol. 7 (1921), No. 26, pp. 98–126.

Oil: The Development of an Oil By-product Industry. Eric K. Rideal *The Chemical Age* (London), Vol. 4 (1921), No. 104, pp. 666–68.

Oil: Estimation of Sulfur by the Lamp Method. F. Esling. *Journal of the Institution of Petroleum Technologists*, Vol. 7 (1921), No. 26, pp. 83–94.

Rubber: The Detection of Accelerators. D. F. Twiss and G. Martin. *India-Rubber Journal*, Vol. 61 (1921), No. 26, pp. 17–18.

Starch: The Manufacture of Starch, Glucose and By-products. R. H. Williams. *Canadian Chemistry and Metallurgy*, Vol. 5 (1921), No. 7, pp. 195–6.

Steel: Solid Solution of Oxygen in Iron. J. E. Stead. *Forging and Heat Treating*, Vol. 7 (1921), No. 6, pp 332–33.

MARKET REPORT—JULY, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		July 1	July 15
Acid, Boric, cryst., bbls	lb.	.13¾	.13¾
Hydrochloric, com'l, 20°	lb.	.01½	.01½
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07¼	.07¼
Phosphoric, 50% tech	lb.	.13	.13
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	18.00	18.00
Oleum 20%	ton	23.00	23.00
Alum, ammonia, lump	lb.	.03¼	.03½
Aluminium Sulfate (iron-free)	lb.	03	.03
Ammonium Carbonate, pwd	lb.	.08	.07
Ammonium Chloride, gran	lb.	.06¾	.06¾
Ammonia Water, carboys, 26°	lb.	.08	.08
Arsenic, white	lb.	.06½	.06½
Barium Chloride	ton	60.00	85.00
Nitrate	lb.	.09	.09
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, works	100 lbs.	2.75	2.75
Borax, cryst., bbls	lb.	06	.06
Bromine, pure	lb.	.27	.27
Calcium Chloride, fused	ton	28.75	28.75
Chalk, precipitated, light	lb.	.04	.04
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.62½	5.62½
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.75	3.50
Lead Acetate, white crystals	lb.	.13	.13
Nitrate	lb.	.15	.15
Red American	100 lbs.	.11¼	.11¼
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	1.40	1.40
Magnesium Carbonate, tech	lb.	.10½	.10
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	46.00	46.00
Phosphorus, yellow	lb.	.30	.30
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.11½	.11½
Bromide, imported	lb.	.18	.18
Carbonate, calc., 80–85%	lb.	.05	.05
Chlorate, cryst	lb.	.09	.08
Hydroxide, 88–92%	lb.	.05	.04½
Iodide, bulk	lb.	2.85	2.75
Nitrate	lb.	.10	.10
Permanganate, U. S. P.	lb.	.27	.27
Salt Cake, bulk	ton	35.00	35.00
Silver Nitrate	oz.	.41	.41½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.25	2.25
Caustic, 76%	100 lbs.	4.25	4.15
Sodium Acetate	lb.	.06	.06
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.08¼	.08
Chlorate	lb.	.07½	.07½
Cyanide	lb.	.20	.20
Fluoride, technical	lb.	.12	.11½
Hyposulfite, bbls	100 lbs.	4.00	3.50
Nitrate, 95%	100 lbs.	2.70	2.50
Silicate, 40°	lb.	.01½	.01½
Sulfide	lb.	.06	.06
Bisulfite, powdered	lb.	.06	.06
Strontium Nitrate	lb.	.12	.12
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride	lb.	.18	.18
Oxide	lb.	.40	.40
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.09	.09

ORGANIC CHEMICALS

		July 1	July 15
Acetanilide	lb.	.27	.26
Acid, Acetic, 28 p. c.	100 lbs.	2.75	2.75
Glacial	lb.	.11	.10
Acetylsalicylic	lb.	.58	.60
Benzoic, U. S. P., ex-toluene	lb.	.65	.65
Carbolic, cryst., U. S. P., drs.	lb.	.10	.10
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	.45	.45
Acid (*Concluded*)			
Oxalic, cryst. bbls	lb.	.18	.18
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.21	.20
Tartaric, crystals, U. S. P.	lb.	.29	.28
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12½	.12½
Alcohol, denatured, complete	gal.	.37	.37
Ethyl, 190 proof	gal.	4.75	4.75
Amyl Acetate	gal.	2.40	2.40
Camphor, Jap, refined	lb.	.73	.77
Carbon Bisulfide	lb.	.06	.06
Tetrachloride	lb.	.10½	.10½
Chloroform, U. S. P.	lb.	.43	.43
Creosote, U. S. P.	lb.	.43	40
Cresol, U. S. P.	lb.	.18	.17
Dextrin, corn	100 lbs.	3.15	2.85
Imported Potato	lb.	.07	.07
Ether, U. S. P., conc., 100 lbs.	lb.	.18	.16
Formaldehyde	lb.	.13½	.13
Glycerol, dynamite, drums	lb.	.13	.12½
Methanol, pure, bbls	gal.	1.25	1.25
Pyridine	gal.	2.75	2.75
Starch, corn	100 lbs.	2.28	2.28
Potato, Jap	lb.	.05	.05
Rice	lb.	.18	.18
Sago	lb.	.04½	.04½

OILS, WAXES, ETC.

		July 1	July 15
Beeswax, pure, white	lb.	.45	.43
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.08½	.08½
Ceresin, yellow	lb.	.12½	.12½
Corn Oil, crude, tanks, mills	lb.	.05½	.05¾
Cottonseed Oil, crude, f. o. b. mill.	lb.	.06	.07
Linseed Oil, raw (car lots)	gal.	.72	.75
Menhaden Oil, crude (southern)	gal.	.30	.30
Neat's-foot Oil, 20°	gal.	1.00	1.00
Paraffin, 128–130 m. p., ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.35	5.40
Rosin Oil, first run	gal.	.40	.40
Shellac, T. N.	lb.	.56	.50
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.09½
Tallow Oil, acidless	gal.	.70	65
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.62	.67

METALS

		July 1	July 15
Aluminium, No. 1, ingots	lb.	.22½	.22½
Antimony, ordinary	100 lbs.	5.00	4.87½
Bismuth	lb.	1.50	1.50
Copper, electrolytic	lb.	.12¾	.12¾
Lake	lb.	.13	.13
Lead, N. Y.	lb.	.04½	.04½
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	65.00	65.00
Quicksilver, flask	75 lbs. ea.	46.00	46.00
Silver, foreign	oz.	.60	.59
Tin	lb.	.29	.29
Tungsten Wolframite	per unit	3.25	3.25
Zinc, N. Y.	100 lbs.	4.75	4.55

FERTILIZER MATERIALS

		July 1	July 15
Ammonium Sulfate, export	100 lbs.	2.50	2.50
Blood, dried, f. o. b. N. Y.	unit	3.50	3.50
Bone, 3 and 50, ground, raw	ton	45.00	45.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	3.50 & .10	3.50 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	11.00	11.00
Tennessee, 78–80%	ton	15.00	15.00
Potassium Muriate, 80%	unit	1.00	.90
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	2.75 & .10	2.75 & .10

COAL-TAR CHEMICALS

		July 1	July 15
Crudes			
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U S. P.	lb.	.18	.17
Cresylic Acid, 97–99%	gal.	.90	.80
Naphthalene, flake	lb.	.08	.08
Phenol, drums	lb.	.10	.09
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.60	.45
Intermediates			
Acids:			
Anthranilic	lb.	1.80	1.50
B	lb.	2.25	2.25
Benzoic tech	lb.	.60	.60
Broenner's	lb.	1.75	1.55
Cleve's	lb.	1.30	1.30
Gamma	lb.	3.25	3.25
H	lb.	1.10	1.15
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.75	2.75
Naphthionic, crude	lb.	.70	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.30	.29
Tobias'	lb.	2.25	2.25
Aminoazobenzene	lb.	1.25	1.25
Aniline Oil	lb.	.19	.18½
For Red	lb.	.42	.42
Aniline Salt	lb	28	26
Anthraquinone	lb.	1.75	1.75
Benzaldehyde, tech	lb.	.45	.50
U. S. P.	lb.	1.50	1.50
Benzidine (Base)	lb.	.90	.90
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	6.00	5.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.45	.42
Dinitrobenzene	lb.	.25	.25
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.60	.60
G Salt	lb.	.80	.80
Hydroquinol	lb	1.35	1.50
Metol (Rhodol)	lb.	4.00	3.00
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.15	2.00
a-Naphthylamine	lb.	.38	.38
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.38	.33
m-Nitroaniline	lb.	.90	.95
p-Nitroaniline	lb.	.85	.75
Nitrobenzene, crude	lb.	.12½	12
Rectified (Oil Mirbane)	lb.	.13¾	.13¾
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.90	.85
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.75	1.75
Phthalic Anhydride	lb.	.55	.50
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.75	.65
Resorcinol, tech	lb.	1.75	1.75
U. S. P.	lb.	2.00	1.75
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.60	.42
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.44	.45
o-Toluidine	lb.	.27	.25
p-Toluidine	lb	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

		July 1	July 15
Acid Colors			
Black	lb.	1.00	1.00
Blue	lb.	1.50	1.50
Acid Colors *(Concluded)*			
Fuchsin	lb.	2.50	2.50
Orange III	lb.	.60	.60
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.85	.85
Direct Colors			
Black	lb.	.90	.90
Blue 2B	lb.	.70	.70
Brown R	lb.	1.65	1.65
Fast Red	lb.	2.35	2.35
Yellow	lb.	2.00	2.00
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	.80	.80
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90
Sulfur Colors			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	1.00	1.00
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	2.80	2.80
Basic Colors			
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.80	80
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	4.50	4.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	2.75	2.75
Methylene Blue, tech	lb.	2.75	2.75
Methyl Violet 3 B	lb.	2.75	2.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	16.00	16.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of

INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society

Editor: CHAS. H. HERTY
Assistant Editor: LOIS W. WOODFORD
Advisory Board: H. E. BARNARD J. W. BECKMAN A. D. LITTLE A. V. H. MORY
CHAS. L. REESE GEO. D. ROSENGARTEN T. B. WAGNER

EDITORIAL OFFICES:
One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613-0614

Cable Address: JIECHEM

ADVERTISING DEPARTMENT:
170 Metropolitan Tower
New York City
TELEPHONE: Gramercy 2145

Volume 13 SEPTEMBER 1, 1921 No. 9

EDITORIALS:

An Acknowledgment 750
Welcome to our Visitors 750
The Fight in the Senate 750
Effective Help 751
The Passing of Secrecy 751
The President Takes a Hand 752
The Meeting and the Exposition 752
Experimental Evidence 752

OUR FOREIGN TRADE IN CHEMICALS. O. P. Hopkins 753

ORIGINAL PAPERS:

A Fermentation Process for the Production of Acetone, Alcohol, and Volatile Acids from Corncobs. W. H. Peterson, E. B. Fred and J. H. Verhulst 757
Alkali Fusions. III-Fusion of Phenylglycine-o-Carboxylic Acid for the Production of Indigo. Max Phillips 759
The Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese. Robert E. Wilson, W. Grenville Horsch and Merrill A. Youtz 763
The Detection of Carbon Monoxide. C. R. Hoover 770
The Determination of Tannin. John Arthur Wilson and Erwin J. Kern 772
The Preparation of Ethylene by Hydrogenation of Acetylene. William H. Ross, James B. Culbertson and J. P. Parsons 775
Viscosity-Temperature Curves of Fractions of Typical American Crude Oils. E. W. Dean and F. W. Lane 779
The Effect of Chemical Reagents on the Microstructure of Wood. Allen Abrams 786
The Detection and Estimation of Coal-Tar Oils in Turpentine. V. E. Grotlisch and W. C. Smith 791
A Revision of the Optical Method for Analyzing Mixtures of Sucrose and Raffinose. C. A. Browne and C. A. Gamble 793
Shortening: Its Definition and Measurement. Clark E. Davis 797

A Process for Producing Palatable Sirup from Sugar Beets. Sidney F. Sherwood 799
A Study of the Oil Bromide Test of Linseed Oil. Thomas A. Davidson 801, 849
The Precipitation of Solid Fatty Acids with Lead Acetate in Alcoholic Solution. E. Twitchell 806
Determination of Metallic Aluminium and of Aluminium Oxide in Commercial Metal. Julian H. Capps 808
A Rapid Method for the Determination of Sodium Chloride in Soap. H. C. Bennett 813
The Application of the Immersion Refractometer to the Analysis of Aqueous Salt Solutions. C. A. Clemens 813
The Influence of Certain Organic Accelerators on the Vulcanization of Rubber. George Stafford Whitby and Osman James Walker 816

LABORATORY AND PLANT:

A Combined Extractor Reflux Condenser, Still and Autoclave. Alfred T. Shohl and Mathilde L. Koch 819
Radiation Effects in Thermometry. Clark S. Robinson 820

ADDRESSES AND CONTRIBUTED ARTICLES:

The Chemistry of Acenaphthene and Its Derivatives. Dorothy A. Hahn and Harriet E. Holmes 822
European Practice in Cellulose Acetate and Dopes during the War. Philip Drinker 831
Motor Fuel from Vegetation. T. A. Boyd 836
The Role of the Chemist in Relation to the Future Supply of Liquid Fuel. Harold Hibbert 841

SOCIAL INDUSTRIAL RELATIONS:

The Science of Human Engineering. H. W. Jordan 844

SCIENTIFIC SOCIETIES:

The New York Meeting; Calendar of Meetings; Seventh National Exposition of Chemical Industries 844

NOTES AND CORRESPONDENCE:

The Detection of Phenols in Water: Assignment of Patents; A Study of the Oil Bromide Test of Linseed Oil 848

MISCELLANEOUS:

Bakelite Company Wins Decree 769
Chemical Laboratory Fire at Tulane University 852
WASHINGTON LETTER 850
LONDON LETTER 851
PARIS LETTER 852
INDUSTRIAL NOTES 853
PERSONAL NOTES 853
GOVERNMENT PUBLICATIONS 854
BOOK REVIEWS 856
NEW PUBLICATIONS 858
MARKET REPORT 859

Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted.
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N.W., Washington, D. C.

EDITORIALS

An Acknowledgment

We have worked in the face of what seemed insurmountable obstacles to place this issue in the hands of our readers promptly on schedule. Its typographical shortcomings are not due to negligence on the part of our staff, for they have worked untiringly, nor through any fault of our printer, who waived his contract terms to permit the editorial sections to be printed elsewhere. Labor conditions unexpectedly intervened, and it was necessary to move the half-finished work bodily from one shop to another in the dead of night. Obviously it was impossible to match accurately the usual type styles, and conformity of detail in the third shop not to be expected. Standards have been sacrificed for promptness. We are heartily grateful to the efficient manager and capable typesetters who "delivered the goods".

Welcome to our Visitors

A hearty welcome to our British and Canadian guests!

It is easy for those of us who think alike, speak alike and feel alike to get together for common good. The editorial suggestion of a year ago that the chemists of Great Britain, Canada and the United States meet together for common counsel met with sympathetic response. Correspondence and personal conferences soon made the matter an accomplished fact. Never was there better illustration of the value of personal acquaintance, and the next two weeks will afford opportunity for a wide extension of this personal contact.

The broad basis of sympathetic understanding in each of these joint meetings now in progress lies not so much in a common language as in the fact that in each of our lands the chemist, before the war, occupied a lowly plane in our body politic. His existence was known but little heeded. He was considered a man apart, no glamor attached to his accomplishments, his opinions were given but scant attention by men in power. In each country the Teuton, through cleverly fostered propaganda, was held in popular esteem as the superman in chemistry.

But the tasks of war were worthily performed. Side by side we worked on those pressing problems upon the successful outcome of which great issues hung. In the light of our accomplishments national gratitude was a not unreasonable expectation. Such a feeling would logically express itself in the form of prompt protective legislation which would safeguard the future. However, in England it was only after a great tide of imports had rushed in through the breach made in the dyke of war blockade by the Sankey decision that the gap was closed by the Licensing Act of December 1920. The British dye industry is still suffering from that devastating flood. Not before August 12, 1921, almost three years after the Armistice, was the Government's Safeguarding of Industries bill, protecting the key industries developed during the war, passed. How like the war psychology! Grave disaster was the stimulus necessary for effective measures of defense. But once aroused the British answer to the call has always been complete.

With us in America the story has been a little different, but the spirit of dallying just as evident. We have made use of the sand bags of the War Trade Board to avoid a break in our dyke against a flood of dyes, though often this temporary expedient has seemed on the point of exhaustion, but in other key industries we still await the enactment of permanent tariff legislation to check the uneven competition of longer experience and depreciated currencies. Again how like war psychology—slow in being aroused to our responsibilities.

That which gives heart and hope to all of us in each of our lands is that public understanding, though gradually, is surely arising, and we believe it a historical fact that when once the Anglo-Saxon race sees a thing clearly it sees it through.

Fortunately the visit is not to be a hurried one, for besides the opportunities of close association afforded by the week of the General Meeting with its formal program there will follow Exposition Week with its numerous occasions for informal gatherings.

While it is hoped that the social functions arranged will afford an atmosphere of good fellowship and happiness, nevertheless the period just before us is pregnant with possibilities of great good, not so much to ourselves as to the lands we love. It is a time for great things. The occasion is here. Unfetter the imagination. Let us plan for the future on broadest lines and unitedly set about to accomplish their fulfillment.

The Fight in the Senate

We call it a fight for that is the only fitting term to describe the hearings on the dye embargo held before the Senate Committee on Finance during the dog days of August 1921. The defeat of the measure in the House by such a heterogeneous vote, secured under a cloud of fake issues, "monopoly," "trusts," "corruption," etc., made certain the reopening of the question in the Senate.

While waiting for the battle to begin the opposition celebrated its victory in the House by a luncheon given in New York City on July 25, 1921, by the American Protective Tariff League in honor of Congressman Frear, the aggressive leader for the German interests. Among the other guests was Mr. Metz, assumedly representing the importers and the Democrats.

With the social festivities ended the hearings began, with the chemical interests, aided strongly by the War and Navy Departments, on the offensive to regain the ground lost in the House, while the importers and the small group of textile interests took up the defensive, Senator Moses occupying a strategic position behind the lines.

Again was covered the same ground so thoroughly thrashed out during December 1919. The outstanding features of the new hearings were the aggressive leadership of General Fries, the Chief of the Chemical Warfare Service, the letters to Senator Penrose by Secretaries Weeks and Denby (reproduced below), the admirable brief filed by Mr. Choate, the presentation of the smaller manufacturers' case by Mr. Isermann, the outspoken opposition to the embargo plan by the Amoskeag Mills (Senator Moses' chief constituent), constant questioning by Senator Smoot, and the presence of former Senator Thomas of Colorado at the hearings.

But the cleverest move in the proceedings was by Chairman Penrose. The Democrats had been called in to the hearings on the American valuation and dye embargo features of the bill. Known to be in opposition, their votes would be helpful in killing both, but Republican sentiment for American valuation developed so strongly that a quandary presented itself. This was easily solved by the Chairman inviting the Democrats out when voting time came. Then the Republican members of the Ways and Means Committee were called in to a joint conference, and American valuation was adopted.

Meanwhile the Senate Committee received from the House the new Longworth measure extending for three months from August 27 the ad interim control of imports of dyes through license by the War Trade Board. The Senate Finance Committee voted favorably upon this bill. As soon as announcement was made of the action of the Committee, eight senators, it is reported, notified Chairman Penrose that they would filibuster against the bill. This did not disturb the wily Chairman at all. His nimble wit readily hit upon a device. The bill was broadened to include all sections of the Emergency Tariff Bill and to extend the time to January 1, 1922, unless repealed by tariff legislation in the meantime. To filibuster against the dye control in this modified bill would mean obstructive tactics against features in which some of the filibusterers are decidedly interested. In this form the bill was reported and it is believed will pass the Senate.

The joint conference of the two committees for permanent tariff legislation for dyes resulted in the appointment of a joint sub-committee consisting of Senators Smoot and Dillingham and Representatives Longworth and Frear, which was instructed to endeavor to devise some form of compromise legislation which would protect the industry and at the same time bring a united and successful vote in the Senate. The committee has not yet reported, though the composition of the committee indicates that if Mr. Longworth can succeed in saving the embargo for which he has so consistently fought, his efforts should entitle him to be considered the legislative genius of the age.

Effective Help

Two highly interesting and significant letters have had a powerful influence in directing public attention to the most important issue at stake and in changing the tide of congressional sentiment toward legislation effectively protecting the American coal-tar chemical industry.

Chairman, U. S. Senate Finance Committee, JULY 26, 1921.
Senate Office Building,
Washington, D. C.

MY DEAR SENATOR PENROSE:

My attention has been drawn to the fact that the Fordney Tariff Bill as passed by the House of Representatives will not protect the American organic chemical industry from destruction by German competition.

One of the most startling discoveries of the World War was the fact that the United States could mobilize, train and equip with clothing three or four million men far quicker than it could supply the cannon, the rifles and the ammunition for them. Notwithstanding that from 1914 to 1917 our great steel industries and our rapidly developing chemical industries had been working feverishly to increase their facilities to supply ammunition and guns to the Allies, it was more than a year after we entered the war before those industries were able to supply ammunition, war gases, guns and rifles to meet American needs. Even then our chemical industries were so undeveloped in 1917 that it was necessary for the Government to build tremendous high explosive plants as at Nitro, West Virginia, and practically all poisonous gas plants for supplying gases and smoke materials to the United States Army.

Prior to the outbreak of the war in Europe in 1914, the American organic chemical industry was very small. This was particularly true of the dye industry. At that time, the value of coal tar dyes, drugs, etc. produced in Germany was more than twice that produced by all the rest of the world, and more than twenty-one times that of the United States. The dye industry is the backbone of the organic chemical industry on which all Governments are dependent for their high explosives, their war gases, their medicines and many other materials.

So fully did Germany realize before, during and after the World War that predominance in the organic chemical industry and particularly the dye industry meant the most valuable measure of preparedness possible, that she has united all her organic chemical industries into one great trust, the Interessen-Gemeinschaft.

Not only is the German workman paid much less than the American workman, but the depreciated mark makes the difference still more pronounced. It, therefore, seems certain that the German dye trust can produce dyes and similar materials so much cheaper than the Americans can produce them that no ordinary tariff can keep the German dye trust from destroying the American dye industry and thereby crippling the whole organic chemical industry.

The use of high explosives and war gases will unquestionably be far greater in any future struggle than in the World War. Inasmuch as the coal tar industry, which is the base of all dyes, is also the base of all high explosives and most of our war gases, it is of the most vital importance to preparedness that the dye industry be developed to the fullest possible extent in this country. It is felt that this danger is so great that I urge the enactment of the embargo feature of the Fordney Tariff Bill as submitted by the Ways and Means Committee of the House as the only way to prevent crushing our chemical market by German competition.

For the above reasons, England, France, Italy and Japan have already enacted embargoes on the importation of dyes, medicinals and other organic chemicals which will remain in effect for varying periods up to ten years in the case of England.

Very truly yours,

(*Signed*) JOHN W. WEEKS
Secretary of War

MY DEAR SENATOR PENROSE: JULY 27, 1921

Understanding that the recommendation of the Ways and Means Committee of the House placing a limited embargo on the importation of coal-tar products (H. R. 7456 General Tariff Revision Page 6) was rejected by the House, I am earnestly requesting that your Committee give special attention to this feature.

The Longworth bill (H. R. 8078 66th Congress) included a selective embargo regulating the importation of organic chemicals particularly those useful in the preparation of explosives and toxic gases used in chemical warfare.

The Fordney bill as reported from the Committee included a modified clause to the same effect. It is of great value to the Navy to encourage the development of chemical activities in the manufacture of all products connected with the above mentioned articles, especially those manufacturers whose establishments can easily be diverted to the manufacture of war materials when needed. The restoration of the embargo clause will be of material help and I will greatly appreciate your assistance to this effect.

Sincerely yours,

(*Signed*) EDWIN DENBY
Secretary of the Navy

The Passing of Secrecy

A notable example of true progressive spirit was furnished at the convention of the Biscuit and Cracker Manufacturers Association held in Atlantic City last June. From the accounts of this meeting the Technical Bureau, provided by this organization for the benefit of its members, had evidently been having some rather rough sledding in prevailing upon the several members to make full use of its possibilities of service. Evidently also the Bureau had been doing some effective work, with the aid of the officials of the Association, in developing a broad-minded spirit of progress among the members, for at the convention a majority agreed to furnish to the Technical Bureau their formulas to be passed on to such members of the Association as requested them. Furthermore it was decided to employ a field man to visit the different factories and give to the members the fullest information on the best methods and latest discoveries in the baking business.

Brought together on this fundamental basis of true progressiveness it was an easy matter to swing an initial appropriation of $300,000 for a national advertising campaign to increase the consumption of the products of the industry, to be continued for several years with expanding appropriations. Then they listened to addresses of value to all by eminent food chemists and received new points of view for betterment of work each in his own factory.

Can anyone doubt that the net outcome of such a gathering is increased prosperity to all? And the price of it was the disclosure to the Technical Bureau of the once prized secret formulas, the guarding of which had proved a brake upon the entire industry.

Is there not food for thought in all of this for the chemical industries? Secrecy has been a part of our inheritance handed down from the age of alchemy, but the days of ultra-secrecy are passing. Not necessarily through a Technical Bureau, nor that fortunate medium which the canners found in their Research Laboratory in Washington, but certainly through some agency which will be found best adapted to the needs of their chemical staffs, a way will be found out of the fog of secrecy which now prevents full steam ahead. He who finds that way will be the true leader and benefactor of the American chemical industry.

The President Takes A Hand

The legal power of the War Trade Board to control by license importations of synthetic organic chemicals was to expire on August 27; unmistakable activity was noticeable in importing circles preparatory to the great day; Mr. Longworth, always on the watch, had introduced a resolution extending the period of this control five months; this had been reported favorably from the Ways and Means Committee, but amended to read three instead of five months.

On August 11 the resolution came up for debate before that same House which only recently had defeated the embargo provision of the tariff bill, but suddenly the atmosphere cleared and the measure was quickly passed, for Mr. Longworth read to the House the following letter from President Harding:

The White House

Washington, August 10, 1921

Hon. Nicholas Longworth,

House of Representatives, Washington, D. C.

My Dear Congressman Longworth: I have your note calling my attention to the fact that the bill extending the provisions of the emergency tariff act relating to the protection of the American dye and chemical industry is to be before the House on the morrow. I am aware that the Secretary of the Treasury has already called the attention of your committee to the extreme desirability of extending this protective provision.

Surely we would be both unmindful and unjust if we failed in a suitable protection of this industry until the new and complete tariff revision act is made effective.

Very sincerely,

(Signed) WARREN G. HARDING

Never was a more complete summing up given than in the three words: "unmindful and unjust." They tell the history of yesterday, the duty of to-day and the danger of to-morrow. The President has plainly saved the day for the Emergency legislation. A still greater debt of gratitude will be owed to him if in the light of the strong letters of the Secretary of War and the Secretary of the Navy he throws his great influence to the preservation of the embargo feature in the permanent legislation, thereby assuring beyond a question the future of the industry.

Mr. Harding is looking far into the future and seeking higher ground than either trade or war. On the same day his letter to Mr. Longworth was made public there was published the text of the formal invitation to the nations to join in a disarmament conference. Evidently both the President and Secretary Hughes have been giving due thought to the question of chemical disarmament, for in the invitation it is stated: "It may also be found advisable to formulate proposals by which in the interest of humanity the use of new agencies of warfare may be suitably controlled," a cautious sentence conveying a conviction of the realities, the difficulties and the necessities of this momentous question. It may be that the President is "thinking it through."

The Meeting and the Exposition

The period, September 6 to 17, 1921, should prove historic for chemistry. Beginning with the Council Meeting on the sixth the Annual Meeting of the **American Chemical Society** will be held in New York City. British and Canadian chemists will join in the sessions. The advance activities of the officers of the Divisions and Sections give promise of scientific programs of unusual value, while for the general meetings with speakers of national and international distinction have been announced.

With a brief intermission for excursions there follows the Seventh National Exposition of Chemical Industries, whose doors will be open from September 12 to 17. The conversion of the Grand Central Palace into an office building made necessary the removal of the Exposition to other quarters. Fortunately, there was found in the Armory of the Eighth Coast Artillery an ideal building. Its floor space is so enormous as to admit of installation of an even greater number of exhibits than in previous expositions, all on one floor. Perhaps this may prove symbolical of greater unification in the industry.

The past year has been a trying one. Chemistry was no exception to the rule in the depression which characterized all lines of industrial effort. But we have carried an additional load of uncertainty as regards the outcome of legislation. The sky is not yet clear, but the clouds are breaking and at any time the sun of prosperity and certain future may break through. If so it will make this great gathering one long to be remembered. Frankly, we are optimistic.

Experimental Evidence

It was in Philadelphia, that city of due decorum, on July 19, 1921, some four years after the use of tear gas for dispersing men engaged in fiercest warfare, that there assembled, despite the prevalent crime wave, some two hundred members of the Police Force, with no sense of the humor of the situation, to determine definitely whether, as an organized group, they could, without gas masks, charge a given point through an atmosphere of one of the most powerful lachrymal gases known. The impossibility of such an accomplishment could readily have been attested to by the merest yardboy at Edgewood Arsenal.

Such conservatism and such slowness to utilize modern weapons suggests the attitude of those thoroughly set and comfortable officers of our Navy who still see no demonstration of anything worth while for their consideration from the recent sinking of a destroyer, a cruiser and a battleship off Hampton Roads by high explosives dropped from airplane squadrons.

Experimental evidence sometimes leads to false conclusions. The doughboys could have given advice based upon actual experience.

OUR FOREIGN TRADE IN CHEMICALS

By O. P. Hopkins 1824 Belmont Road, Washington, D. C.

The world-wide depression that overtook business during the fiscal year 1920-21 did not spare our foreign trade in chemicals and allied products. Here and there is to be found a commodity that apparently has not suffered seriously, but statistics for the year are likely to be misleading in such cases.

There are economists who say "I told you so" when the great slump is mentioned, but they certainly were not vociferous before the event. Looking backwards, it is evident that one of the chief causes of the severity of the depression was the old lack of scientific direction of production. While orders pour in, production is speeded up in every direction with no tally kept of total production or thought given to its relation to the possible consumption. After a brief boom period of high prices comes a buyers' strike, or at any rate overproduction—then the depression.

On paper the foreign trade in chemicals was not hit so hard during the fiscal year just closed as were some other classes of commodities. A rough estimate indicates a total export of all chemicals and allied products of about a billion dollars in 1921, against something like a billion and a quarter in 1920. The decrease in imports was relatively about the same. Exports of chemicals proper, however, decreased 30 per cent, drugs, medicines, etc., about 25 per cent, and dyes nearly 27 per cent, in value, in value. Any but the most pessimistic will be encouraged by the fact that the 1921 values are still greatly in excess of those for 1914. The slump is merely from the boom year:

Summary of Foreign Trade in Chemicals and Allied Products
(In Millions of Dollars)

Classes	Imports 1914	Imports 1920	Imports 1921	Exports 1914	Exports 1920	Exports 1921
Chemicals	72	96	101	15	92	64
Drugs, medicines, etc.	9	22	22	11	41	31
Dyes, dyewoods	10	6	8	(2	26	19
Explosives	1	2	1	6	28	46
Fertilizers	28	39	29	12	33	25
Gums, resins, etc.	88	330	153	20	37	22
Oils, fats, waxes	75	319	201	194	607	613
Paints, pigments, etc.	2	2	3	7	27	21
Tanning materials	5	12	9	1	6	2
Paper and pulp	30	106	159	6	33	27
Miscellaneous products[3]	120	701	689	44	324	181
Miscellaneous materials	8	9	11	2	4	4
Total	448	1644	1386	318	1258	1055

[3] The importance of this class is due to the inclusion of sugar. The article s making up this class are shown in the detailed table of miscellaneous products.

In the more detailed tables that follow, quantities have been given wherever possible, as values have since 1914 been comparatively worthless for purposes of comparison. All compilations are based upon statistics of the Department of Commerce, Washington, D. C.

The Trade in Chemicals

With a few exceptions the trade in chemicals slumped in 1921 as compared with 1920. Even where there is apparently only a slight falling off it should be borne in mind that the market may have been affected too late in the year to make an impression on the year's total.

The exports of acids fell off in 1921, but as a whole were above those of 1914. Sulfuric acid shipments have fallen from 68,000,000 pounds in 1918 to 32,000,000 in 1920, to 18,000,000 in 1921, but are still 6,000,000 above 1914. Imports of acids are also declining but are still above the figures for 1914.

The exports of caustic soda were cut in half during 1921, and shipments of sodium silicate decreased about one-third. There was only a slight decrease in foreign sales of sal soda, and the exports of soda ash actually increased in value, although the quantity shipped was slightly below that of 1920. The falling off in the value of "all other" soda exports was about one-third. Imports of sodium nitrate decreased from 907,000 to 844,000 tons; the 1914 imports totaled 564,000 tons.

The exports of potassium chlorate and other non-fertilizer potash salts were cut in half in 1921. Imports of potassium carbonate fell off from 22,000,000 to 14,000,000 pounds, as compared with 20,000,000 pounds in 1914. The imports of potassium nitrate went up from 27,000,000 pounds in 1920 to 31,000,000 in 1921. In 1914 the total importation was only 3,500,000 pounds.

An increase occurred in the exports of chloride of lime from 31,000,000 to 37,000,000 pounds. Imports also showed an increase—from less than 1,000,000 to more than 4,000,000 pounds, but the total imports in 1914 amounted to 47,000,000 pounds.

The growth in the imports of cyanides is shown by the fact that about 15,000,000 pounds of potassium cyanide was purchased in 1921, more than three times the figure for 1920 and fifteen times the imports in 1914. Sodium cyanide was not shown in the statistics for 1914, but the imports in 1921 were only slightly under those in 1920 and worth over a million dollars.

Of the coal-tar crudes, benzene was exported to the extent of 67,000,000 pounds in 1921, a big increase over the 17,000,000 recorded for 1920. The value of other crudes exported increased slightly. Imports of creosote oil rose from 8,000,000 gallons in 1920 to 28,000,000 in 1921. The 1914 imports totaled nearly 61,000,000 gallons.

The expansion in the domestic production of sulfur during the war is reflected in the disappearance of imports since. Exports, on the other hand, fell off only slightly in 1921 as compared with 1920, but the industry suffered during the second half of the year.

Trade in Chemicals, Drugs, Dyes, Etc.

Articles Imports	1914	1920	1921
Acids (except coal tar acids):			
Oxalic, lbs.	8,507,850	1,401,547	2,058,907
All other, value	$1,133,252	$4,004,018	$2,587,571
Albumin, egg, lbs.	(1)	8,956,845	7,889,411
Ammonia, muriate, lbs.	9,176,729	5,344,028	4,417,162
Argols, lbs.	29,793,911	23,638,337	26,485,760
Arsenic or orpiment, lbs.	4,432,793	6,470,700	8,801,293
Balsams, not containing alcohol, lbs.	(1)	745,151	452,167
Calcium, acetate, crude chloride, carbide and nitrate, lbs.		76,845,476	111,261,888
Chemical and medicinal compounds, n. e. s.:			
Alkalies, alkaloids, preparations, mixtures, etc., lbs.	(	6,907,035	11,206,926
Medicinal preparations (see also coal-tar products), value	$1,031,054	$562,586	$1,030,551
All other	(	$1,388,577	$1,316,937
Cinchona bark, and alkaloids or salts of:			
Barks, cinchona, or other from which quinine may be extracted, lbs.	3,648,868	5,242,724	3,567,010
Quinine, sulfate of, and all alkaloids or salts of cinchona bark, oz.	2,879,466	4,580,807	3,630,063

---

[1] The term "chemicals" is here used in the usual restricted sense, as not including drugs, medicines, and dyes.

[2] $400,000

Trade in Chemicals, Drugs, Dyes, Etc., (*Concluded*)

Coal-tar products:			
Crudes			
Acid, carbolic, lbs	8,392,995	157,319	183,709
Benzol, lbs	(1)	170,519	1,717,936
Cresol, lbs	(1)	8,188,303	6,476,140
Creosote oil, gal	60,900,435	8,338,761	27,779,736
Naphthalene, lbs	(1)	6,113,858	13,925,850
Tar and pitch, bbls	(1)	20,607	15,965
Toluol, lbs	(1)	1,195,706	....
All other crudes, value	(1)	$65,818	$159,421
Intermediates			
Acids			
Carbolic (phenol), lbs	(1)	30	1,260
All other, lbs	(1)	11,512	549
Aniline oil, lbs	(1)	(1)	220
Aniline salts, lbs	3,184,467	....	4
All other intermediates	(1)	$217,653	$885,911
Finished products			
Alizarin and dyes, lbs	2,633,414	257,841	352,173
Colors or dyes, n. e. s., value	$7,241,406	$3,775,216	$5,081,970
Indigo, synthetic, lbs	8,125,211[2]	1,014,100	276,849
Medicinal preparations	(1)	$112,611	$236,656
Other finished products	(1)	$79,216	$82,232
All other coal-tar products, value	$1,636,750	....	...
Extracts and decoctions for dyeing, lbs	(1)	1,581,534	708,640
Extracts for tanning:			
Quebracho, lbs	93,329,087	154,944,717	110,194,308
All other, lbs	8,710,040	7,380,920	9,712,978
Fusel oil and butyl alcohol, lbs	5,802,369	6,196,179	1,083,336
Glycerol, crude, lbs	36,409,619	15,656,463	11,118,149
Indigo, natural, lbs	(1)	126,539	147,835
Iodine, lbs	195,087	523,313	595,058
Lactarene, lbs	10,798,614	24,039,313	14,179,764
Licorice root, lbs	115,636,131	48,045,373	59,693,462
Lime, chloride of, lbs	47,423,651	830,207	4,696,773
Citrate of, lbs	3,097,265	10,431,314	5,071,504
Magnesite, not purified, tons	289,494,316	27,503	50,352
Opium, containing 9 per cent or more morphine, lbs	455,200	628,896	77,444
Perfumeries, cosmetics, etc., value	$2,309,027	$5,545,606	$7,078,985
Potash (not for fertilizer):			
Carbonate, lbs	20,603,593	22,147,554	14,774,581
Cyanide, lbs	808,721	5,175,608	13,353,268
Hydrate, not over 15 per cent caustic soda, lbs	8,450,402	782,477	4,934,697
Nitrate, lbs	3,516,580	26,862,012	30,868,786
All other, lbs	5,775,588	2,198,178	4,512,402
Soda:	1914	1920	1921
Cyanide, lbs	(1)	8,629,502	7,742,063
Nitrate, tons	564,049	907,041	843,756
All other salts of, value	$487,038	$1,642,589	$1,343,641
Sulfur, tons	19,389	47	2
Sumac, lbs	10,770,340	21,180,414	2,727,006
All other chemicals, drugs, dyes, etc., value	$13,676,032	$19,076,123	$16,955,157
Exports			
Acids:			
Carbolic, lbs	(1)	2,223,205	659,890
Nitric, lbs	(1)	820,517	267,119
Picric, lbs	(1)	8,073	3,730
Sulfuric, lbs	12,131,750	32,336,893	18,600,704
All other, value	$357,035	$5,291,987	$3,029,332
Alcohol, wood, gal	1,598,476	687,008	467,763
Calcium carbide, lbs	32,845,649	21,164,404	20,147,753
Coal tar, bbls	22,150	81,640	128,103
Coal-tar distillates, n. e. s.:			
Benzol, lbs	(1)	17,282,368	66,622,862
All other, value	(1)	$3,611,514	$4,101,129
Copper sulfate, lbs	7,375,775	4,511,724	4,297,378
Dyes and dyestuffs:			
Aniline dyes, value	(1)	$17,130,397	$13,577,788
Logwood extract, value	(1)	$1,832,231	$1,471,040
All other, value	$356,919[3]	$6,829,937	$3,571,309
Extracts for tanning, value	$639,941	$6,016,438	$1,732,198
Formaldehyde, value	(1)	$2,289,217	$1,376,281
Glycerol, lbs	36,409,619	2,257,623	1,388,194
Infants' food, value	(1)	$3,032,330	$1,520,259
Lime, acetate of, lbs	68,160,224	32,885,132	12,845,700
Chloride of, lbs	(1)	31,252,379	37,425,093
Medicinal and pharmaceutical preparations, value	$6,721,978	$20,118,271	$18,038,328
Perfumery and cosmetics, value	$2,309,027	$7,979,237	$6,236,766
Petroleum jelly, value	$661,889	$3,156,286	$2,072,595
Potash:			
Chlorate, lbs	(1)	2,845,858	1,130,771
All other, value	(1)	$3,362,827	$1,309,852
Roots, herbs, barks:			
Ginseng, lbs	224,605	220,970	157,351
All other, value	$513,071	$1,793,064	$836,320
Soda:			
Bicarbonate, lbs	(1)	11,998,510[4]	13,353,769
Borax, lbs	(1)	10,943,110[4]	4,368,880
Caustic, lbs	(1)	229,684,163	101,021,827
Sal soda, lbs	(1)	12,763,399	10,376,424
Silicate, lbs	(1)	33,692,535	23,099,660
Ash, lbs	(1)	115,997,980	113,481,062
All other salts of, value	(1)	$7,471,808	$5,378,899
Sulfur, tons	110,022	393,404	375,826
All other chemicals, etc., value	$9,019,582	$42,573,500	$24,458,856

[1] Not stated separately.

[2] Stated as "Indigo, natural or synthetic" in 1914, but was probably largely synthetic.

[3] Represents the total value of all dyes and dyestuffs in 1914.

[4] Period from Jan. 1 to June 30, 1920.

Drugs, Medicines and Toilet Preparations

The trade in the products under this head seems to have held up pretty well in 1921. Exports of medicinal and pharmaceutical preparations fell off somewhat in value, but differences in prices could easily account for the drop. The total was still three times what it was in 1914. Receipts of cinchona bark and salts fell off perhaps a quarter in value, and the total is now about what it was before the war. Imports of coal-tar medicinals doubled from 1920 to 1921. Exports of perfumery and cosmetics fell off about 20 per cent in value, although still three times the total for 1914. Imports of such goods, however, increased about 20 per cent in value and were three times as great as before the war. (See table "Trade in Chemicals, Drugs, Dyes, etc.")

Dyes

Exports of aniline dyes decreased in value from $17,130,000 to $13,578,000 from 1920 to 1921. There was also a decrease from $6,830,000 to $3,571,000 in the exports of "All other" dyes and dyestuffs, which include synthetic dyes other than aniline. It is not possible to say just how price changes have affected these totals, but it is evident that competition from Europe is making itself felt in our foreign markets. The only country to take a notably increased amount of dyes from this country in 1921 was China, with a total of $4,809,000 as compared with $3,053,000 in 1920. Slight increases are shown for Brazil, Peru, Dutch East Indies, and Australia. There was an alarming drop in shipments to Japan from $6,727,000 in 1920 to $1,341,000 in 1921, which is attributed partly to renewed German activity and partly to distress in the textile industries. Exports to India dropped from $3,334,000 to $1,834,000. With imports it is a somewhat different story, for there was an increase from $3,775,000 to $5,082,000 in the important class, "Colors or dyes, not elsewhere specified," but there is comfort in the fact that imports of synthetic indigo fell from 1,014,000 to 277,000 pounds. In 1914 the imports of indigo amounted to 8,125,000 pounds. (Details of the dey trade are shown in "Trade in Chemicals, Drugs, Dyes, etc." and the dyewoods are mentioned in "Trade in Miscellaneous Materials.")

Tanning Materials

Imports of tanning extracts fell off 25 per cent in 1921 as compared with 1920, but were still about 8 per cent above the 1914 figure in quantity. Purchases of quebracho wood fell off slightly from 1920, the quantity, however, being less than half of the total for 1914. Imports of mangrove bark went up from 2544 tons to 7156 tons, which is practically the figure given for 1914. Exports of tanning bark were under the figure for 1920, but the item is insignificant. There was a noteworthy falling off of over 70 per cent from the $6,000,000 worth of tanning extract exported in 1920. (See table "Trade in Chemicals, Drugs, Dyes, etc.," for extracts, and "Trade in Miscellaneous Materials" for bark and wood.)

Fertilizers

The imports of potash fertilizers are still further below the pre-war normal than they were in 1920, as the next table will show. Exports of phosphate increased 20 per cent in quantity compared with 1920, but are still about 36 per cent below the figure for 1914. Exports of superphospate, on the other hand, were only a third of the total for 1920. Shipments of ammonium phosphate showed a gratifying increase, but the sales of "all other" fertilizers were cut in half.

TRADE IN FERTILIZERS

ARTICLES Imports	1914	1920	1921
Ammonium sulfate, tons	83,377	2,587	2,537
Bone dust, ash, and meal, tons	41,450	7,340	27,413
Calcium cyanamide, tons	(1)	84,678	34,696
Guano, tons	21,887	18,796	37,570
Kainite, tons	541,846	274,761	204,834
Manure salts, tons	261,342	249,348	123,273
Potash, n. e. s.:			
Muriate, tons	237,886	110,324	49,911
Sulfate, tons	45,139	6,356	12,081
All other substances used only as fertilizer, value	$6,199,554	$4,757,066	$5,406,764
Exports			
Phosphate rock:			
High-grade pebble rock, tons	475,335	351,352	274,953
Land pebble, tons	1,000,630	395,581	651,749
All other, tons	1,906	30,348	16,862
Superphosphates, tons	(1)	93,432	29,954
Ammonium sulfate, tons	(2)	17,489	65,915
All other fertilizers, tons	61,601	239,091	108,431

[1] Not stated separately.

[2] Included in "all other fertilizers" prior to May 1, 1920.

GUMS, RESINS AND NAVAL STORES

Copal, kauri, and damar held their own in the import trade for 1921, but there were substantial decreases in other items of this class. Purchases of rubber fell from 632,000,000 to 357,000,000 pounds, or over 43 per cent.

The export trade in naval stores is only about half what it was in 1914 in quantity, although the sales of turpentine spirits increased 30 per cent in 1921 over 1920. Rosin exports were down one-third from 1920.

TRADE IN GUMS, RESINS, AND NAVAL STORES

ARTICLES Imports	1914	1920	1921
Camphor:			
Crude, natural, lbs	3,476,908	4,025,517	2,092,886
Refined and synthetic, lbs	566,106	1,685,633	812,865
Chicle, lbs	8,040,891	9,699,863	8,710,393
Copal, kauri, damar, lbs	32,693,412	44,480,033	44,617,913
Gambier, lbs	14,936,129	10,207,013	6,292,780
Gum arabic, lbs	(1)	6,718,308	4,416,465
Shellac, lbs	16,719,756	34,151,209	23,871,866
Other gums, lbs	....	14,641,434	10,822,198
India rubber, etc.:			
Balata, lbs	1,533,024	2,013,737	1,879,990
Guayule gum, lbs	1,475,804	1,314,913	995,123
Gutta joolatong, lbs	24,926,571	18,392,164	6,774,189
Gutta-percha, lbs	1,846,109	6,496,309	4,575,392
India rubber, lbs	131,995,742	632,392,636	356,975,223
India-rubber scrap, lbs	25,958,261	14,236,098	6,042,565
Exports			
Naval stores:			
Rosin, bbls	2,417,950	1,321,535	877,160
Tar, turpentine, pitch, bbls	351,352	61,826	41,864
Turpentine, spirits of, gal	18,900,704	7,461,455	9,741,711

[1] Not stated separately.

OILS, FATS AND WAXES

The trade in vegetable oils fell off very badly in 1921 from the boom figures for 1920. Imports were only about a third in value of what they were the previous year, and the export trade was just about as badly hit. On the other hand, the imports of mineral oils doubled in value, while the exports increased 25 per cent.

SUMMARY OF TRADE IN OILS

ARTICLES Imports	1914	1920	1921
Oils:			
Animal	$1,034,000	$3,629,000	$1,388,000
Mineral	13,666,000	41,050,000	81,865,000
Fixed vegetable	28,829,000	141,023,000	50,039,000
Essential	3,492,000	9,439,000	5,570,000
Oil-bearing materials:			
Castor beans	1,139,000	3,674,000	1,302,000
Copra	2,395,000	14,971,000	9,951,000
Flaxseed	10,571,000	76,845,000	9,133,000
Peanuts	1,899,000	12,382,000	2,371,000
Exports			
Oils:			
Animal	822,000	3,426,000	603,000
Mineral	152,174,000	426,349,000	535,560,000
Fixed vegetable	15,624,000	96,226,000	37,017,000
Essential	628,000	2,230,000	1,177,000

The most striking development in the vegetable oil trade was the collapse of the business built up in 1920 in such Oriental oils as coconut, soy-bean, and peanut. Imports of coconut oil totaled 272,000,000 pounds in 1920 and 141,000,000 pounds were exported. In 1921 the imports were down to 165,000,000 pounds while the exports had practically disappeared. Imports of copra were fairly well maintained for the year as a whole. Imports of soy-bean oil reached 196,000,000 pounds in 1920 (which was far below the 1918 figure), and nearly 68,000,000 pounds were exported. In 1921 the imports had dropped to 50,000,000 pounds and the exports to a mere 5,000,000 pounds. The imports of these oils, however, are greatly in excess of the pre-war normal. Cottonseed oil, which was purchased abroad to the extent of nearly 25,000,000 pounds in 1920, was practically removed from the import column in 1921, whereas the exports of this typically American product actually increased from 160,000,000 pounds in 1920 to 283,000,000 pounds in 1921. This is much above the 1914 level.

TRADE IN OILS, FATS, AND WAXES

ARTICLES Imports	1914	1920	1921
Oils, animal:			
Cod and codliver, gal	1,393,706[1]	1,943,357	1,224,660
All other, gal	1,488,973	1,294,134	745,984
Oils, mineral:			
Crude, gal	773,052,480	2,826,860,902	5,607,124,270
Refined			
Benzene, gasoline, naphtha, gal	16,139,912	22,037,592	35,642,815
All other, gal	1,945,007	59,851,312	95,548,796
Oils, fixed vegetable:			
Chinese nut, gal	4,932,444	10,613,638	4,439,981
Cocoa butter or butterine, lbs	2,838,761	41,500	915,177
Cocoanut, lbs	74,386,213	271,539,548	165,268,503
Cottonseed, lbs	17,293,201	24,164,821	1,315,265
Linseed, gal	192,282	4,550,391	1,996,586
Olive, non-edible, gal	763,924	216,145	261,689
Olive, edible, gal	6,217,560	6,812,596	4,443,407
Palm, lbs	58,040,202	50,165,387	31,076,224
Palm-kernel, lbs	34,327,606	53,508	2,769,144
Peanut, gal	1,337,136	22,064,363	2,421,704
Rape-seed, gal	1,464,265	1,229,526	1,171,930
Soy-bean, lbs	16,362,452	195,773,594	49,330,645
All other, value	$439,009	$2,974,966	$791,654
Oils, distilled and essential:			
Birch tar and cajeput, value	(2)	$20,019	$1,829
Lemon, lbs	385,959	870,170	626,014
All other, value	$2,633,789	$8,370,317	$4,989,374
Oleostearin, lbs	5,243,553	1,307,837	742,908
Paraffin (except oil), lbs	7,495,459	8,687,728	5,714,653
Wax:			
Beeswax, lbs	1,412,200	3,923,687	2,215,332
Mineral, lbs	8,086,422	2,816,700	4,755,396
Vegetable, lbs	4,255,686	9,949,567	6,235,416
Grease and oils, n. e. s., lbs	22,322,492	42,165,287	35,106,716
Oil seeds and nuts:			
Castor beans, bu	1,030,543	1,416,328	660,215
Cocoanuts in shell, value	$2,133,416	$4,830,548	$2,690,723
Copra, lbs	45,437,155	218,521,946	196,635,315
Flaxseed, bu	8,653,235	23,391,934	16,170,415
Peanuts			
Not shelled, lbs	17,472,631	12,067,998	5,361,196
Shelled, lbs	27,077,158	120,344,425	42,628,034
Exports			
Oils, animal:			
Fish, gal	448,366	1,310,478	118,261
Lard, gal	110,199	130,635	89,303
All other, gal	891,035	1,452,489	340,329
Oils, mineral:			
Crude, gal	146,477,342	356,542,830	355,200,756
Refined or manufactured:			
Fuel and gas, gal	475,143,205	685,738,142	861,419,680
Illuminating, gal	1,157,283,310	914,137,071	833,194,727
Lubricating, gal	196,884,696	339,701,134	333,902,780
Gasoline, gal	151,611,537	294,949,121	382,610,683
Other naphthas, gal	40,840,730	185,265,961	259,603,571
Residuum, gal	113,370,245	48,300,361	9,825,633
Oils, fixed vegetable:			
Cocoa butter, lbs	(2)	11,048,416	3,170,617
Cocoanut oil, lbs	(2)	141,063,943	6,639,055
Corn, lbs	18,281,576	12,482,679	6,919,170
Cottonseed, lbs	192,963,079	159,400,618	283,268,025
Linseed, gal	239,198	1,136,585	561,277
Peanut, lbs	(2)	4,922,781	1,594,643
Soy-bean, lbs	(2)	67,781,974	5,117,605
All other, value	$338,956	$3,258,446	$1,013,541
Oils, distilled and essential:			
Peppermint, lbs	117,809	90,255	50,425
All other, value	$230,557	$1,551,992	$890,472
Grease:			
Lubricating, value	$2,394,918	$6,157,323	$6,851,936
Soap stock, etc., value	$5,046,959	$8,994,603	$8,994,603
Oleo oil, lbs	97,017,065	74,529,394	106,414,800

Trade in Oils, Fats and Waxes (*Concluded*)

Oleomargarine, lbs	2,532,821	20,952,180	6,219,165
Paraffin:			
Unrefined, lbs	186,357,728	79,023,341	50,121,130
Refined, lbs	(²)	81,784,255	203,289,734
Stearin:			
Animal, lbs	2,724,182	22,505,602	19,177,311
Vegetable, lbs	(²)	5,138,225	1,716,313
Wax:			
Beeswax, lbs	96,215	641,357	189,616
Manufactures of, value	$112,193	$1,203,471	$848,425
Oil seeds and nuts:			
Cottonseed, lbs	16,342,384	3,505,118	4,811,313
Flaxseed, bu	305,546	24,044	1,481
Peanuts, lbs	8,054,817	14,137,956	13,149,417

Period from Oct. 3, 1913, to June 30, 1914.

[2] Not stated separately.

ORES AND METALS

The following data on the trade in ores and metals is not included in the summary table at the beginning of the article, but may be of interest to certain branches of the chemical industry. The figures apply only to ores and metals not advanced beyond the bar and ingot stage.

SUMMARY OF TRADE IN PRINCIPAL METALS

ARTICLES	1914	1920	1921
Imports			
Antimony	$696,000	$1,284,000	$937,000
Chromate of iron	737,000	1,419,000	1,689,000
Copper	54,506,000	94,310,000	61,866,000
Iron	11,879,000	12,221,000	12,215,000
Lead	2,057,000	6,817,000	10,[illegible]43,000
Manganese	1,841,000	8,086,000	10,200,000
Nickel	6,110,000	6,848,000	4,971,000
Platinum	3,976,000	6,990,000	6,282,000
Tin	39,422,000	93,145,000	53,248,000
Tungsten ore	114,000	2,589,000	468,000
Zinc	616,000	965,000	1,361,000
Exports			
Aluminium	1,102,000	5,195,000	4,107,000
Bauxite concentrates	616,000	1,709,000	1,067,000
Copper	149,480,000	127,996,000	73,199,000
Ferrovanadium	503,000	254,000	916,000
Iron	6,261,000	14,454,000	11,238,000
Lead	2,610,000	4,207,000	1,275,000
Nickel	9,404,000	1,144,000	57,000
Tungsten and ferrotungsten	.	58,000	2,000
Zinc	995,000	22,927,000	3,469,878

MISCELLANEOUS PRODUCTS

A better idea of the general depression in foreign trade can be gained from a study of the following table of miscellaneous products than from any of the other tables in this article. In nearly all cases there has been a falling off from 1920. A notable exception is gunpowder, for which there is recorded an increase from less than 2,000,000 pounds to nearly 42,000,000 pounds. Glassware did practically as well in 1921 as in 1920, so far as value is concerned, and the export total for this item is very much higher than in 1914.

TRADE IN MISCELLANEOUS PRODUCTS

ARTICLES	1914	1920	1921
Imports			
Collodion, and manufactures of, value	$569,763	$82,940	$168,442
Explosives:			
Fulminates, gunpowder, etc., value	$256,379	$1,523,553	$189,524
All other value	$600,958	$765,412	$759,347
Glass and glassware, value	$8,191,833	$3,582,403	$11,771,538
Glue and glue size, lbs	22,714,877	1,410,194	3,561,831
Matches, value	$882,812	$1,096,982	$954,898
Oilcloth for floors:			
Linoleum, sq. yds	3,724,086	522,999	825,105
Oilcloth, sq. yd	340,288	62,372	44,763
Paints, pigments, etc., value	$2,325,222	$1,975,769	$2,943,942
Paper and pulp:			
Printing paper			
Not over 8 c. per lb., lbs	536,815,288[1]	1,322,890,825	1,475,111,157
All other, lbs	6,053,429	1,371,576	4,219,925
Surface-coated paper, lbs	6,925,505	369,211	1,157,819
Wrapping paper, lbs	36,515,554	4,983,817	7,444,611
Wood pulp			
Mechanical, tons	177,484	194,119	167,093
Chemical, unbleached, tons	302,963	443,867	349,170
Chemical, bleached, tons	88,917	88,564	107,904
Photographic goods:			
Dry plates, value	(²)	$25,808	$78,452
Motion-picture films			
Not exposed, lin. ft	44,717,323[3]	46,485,434	134,118,621
Negatives, lin. ft	402,704[4]	1,417,774	2,121,593
Positives, lin. ft	20,057,144	3,327,566	5,253,413
Other films and plates, value	$324,535	$1,355,832	$2,724,320
Imports			
Soap:			
Castile, lbs	4,622,082	2,352,974	1,808,872
All other, value	$460,485	$192,103	$319,647

[1] Valued at not above 5 cents a pound prior to April 24, 1920

[2] Not stated separately.

[3] From Oct. 3, 1913, to June 30, 1914.

[4] Stated as "All other" motion-picture films in 1914.

Trade in Miscellaneous Products (*Concluded*)

ARTICLES	1914	1920	1921
Sugar and molasses:			
Molasses, gals	51,410,271	154,670,200	113,413,681
Sugar			
Beet, lbs	2,367,708	14,270,114	22,491,771
Cane, lbs	5,061,564,621	7,577,698,325	6,984,195,691
Exports			
Baking powder, lbs	2,725,964	5,595,126	3,491,666
Blacking and polishes, value	$649,395	$2,845,110	$2,072,963
Candles, lbs	3,047,756	7,691,420	3,252,838
Celluloid and manufactures, value	$1,387,541	$10,044,242	$4,281,709
Chewing gum, value	$178,630	$2,617,483	$1,510,679
Explosives:			
Cartridges, loaded, value	$3,521,533	$9,729,937	$3,099,947
Dynamite, lbs	14,464,601	12,566,057	11,878,600
Fuses, value	(¹)	$709,662	$512,030
Gunpowder, lbs	989,385	1,721,991	43,485,291
Shells and projectiles, loaded, value	(¹)	$12,295,519	$563,966
All other, value	$916,280	$2,250,566	$1,445,610
Flavoring extracts and fruit juices, value	(¹)	$1,425,380	$1,236,135
Glass and glassware, value	$3,729,623	$25,906,621	$25,387,607
Glucose and grape sugar:			
Glucose, lbs	162,680,378	219,793,235	125,972,386
Grape sugar, lbs	36,850,496	25,839,015	15,981,960
Glue, lbs	2,351,770	13,141,294	5,991,872
India-rubber manufactures, value	$12,441,220	$69,226,716	$59,565,572
Ink:			
Printers', value	$443,377	$1,590,096	$1,550,548
All other, value	$181,697	$836,436	$774,423
Matches, value	$77,[illegible]36	$558,911	$389,064
Metal polish, value	$162,504	$451,934	$346,104
Mucilage and paste, value	$95,013	$654,827	$601,263
Oilcloth:			
For floors, sq. yds	163,214	2,623,060	1,287,649
All other, value	$666,479	$2,475,699	$2,917,099
Paints, pigments, etc.:			
Dry colors			
Carbon, bone, and lampblack, value	$421,548	$1,959,208	$1,829,987
All other, value	$690,836	$2,991,618	$2,170,237
Lead			
Red, lbs	(¹)	3,027,731	2,046,339
White, lbs	16,845,154	34,441,918	17,408,803
Ready-mixed paints, gal	852,910	2,553,091	2,317,630
Varnish, gal	1,069,501	1,529,592	1,158,025
Zinc oxide, lbs	29,197,790	30,925,983	10,149,360
All other, value	$1,779,863	$7,756,076	$5,947,461
Paper and pulp:			
Newsprint, lbs	88,966,738	123,335,408	64,156,772
Other printing paper, lbs	28,602,134	92,076,860	78,621,553
Wrapping paper, lbs	14,133,097	65,163,463	42,454,760
Writing paper and envelopes, value	$1,179,232	$7,322,859	$8,232,318
Wood pulp, tons	13,481	33,972	27,168
Photographic goods:			
Motion-picture films			
Not exposed, lin. ft	155,359,550	90,398,122	53,814,601
Exposed, lin. ft	32,690,104	188,527,165	154,931,010
Other sensitized goods, value	$1,348,216	$4,960,928	$5,726,611
Soap:			
Toilet or fancy, value	$2,141,633	$6,625,259	$4,182,428
All other, lbs	58,547,763	155,891,586	85,830,216
Sugar and molasses:			
Molasses, gal	1,002,441	7,667,830	5,348,202
Sirup, gal	11,630,528	12,278,246	4,606,261
Sugar, refined, lbs	50,895,726	1,444,030,665	582,698,488
Vulcanized fiber and manufactures of, value	$854,642	$1,859,357	$2,295,457
Washing powder and fluids, lbs	12,761,958	6,217,201	4,021,497

[1] Not stated separately.

MISCELLANEOUS MATERIALS

The export and import trade in a number of materials that could not conveniently be grouped elsewhere is shown in the following table:

TRADE IN MISCELLANEOUS MATERIALS

ARTICLES	1914	1920	1921
Imports			
Asphaltum and bitumen, tons	180,689	93,397	134,280
Blood, dried, value	$391,816	$678,307	$290,609
Bones, hoofs, horns, value	$1,061,466	$1,754,892	$2,936,889
Dyewoods, crude state:			
Logwood, tons	30,062	45,073	56,977
All other, tons	7,663	3,358	4,846
Fish sounds, lbs	(¹)	79,679	127,784
Gelatin, unmanufactured, lbs	2,341,317	1,121,117	2,396,645
Hide cuttings and other glue stock, lbs	2,158,514[2]	26,248,159	36,104,659
Moss and seaweed:			
Crude, value	$301,259	$457,073	$505,808
All other, value	$54,376	$40,711	$47,195
Rennets, value	$129,720	$159,039	$72,092
Salt, 100 lbs	3,076,071	1,756,240	2,486,091
Tanning materials, crude:			
Mangrove bark, tons	7,689	2,544	7,156
Quebracho wood, tons	73,956	33,672	32,901
All other, value	$468,230	$2,757,859	$1,393,058
Vanilla beans, lbs	897,100	1,130,336	986,071
Exports			
Asphaltum:			
Unmanufactured, tons	49,831	47,024	43,630
Manufactures of, value	$362,347	$682,753	$781,947
Barks for tanning, tons	(¹)	513	382
Moss, value	$51,006	$141,000	$62,595
Salt, 100 lbs	1,489,312	2,574,937	2,426,321

[1] Not stated separately.

[2] Quantity not given for 1914

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single solumn of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, e. g., sulfur, per cent, gage, etc.

A Fermentation Process for the Production of Acetone, Alcohol, and Volatile Acids from Corncobs

By W. H. Petersan, E. B. Fred and J. H. Verhulst

DEPARTMENTS OF AGRICULTURAL CHEMISTRY AND AGRICULTURAL BACTERIOLOGY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The production of acetone by biochemical methods in England and Canada during the war was carried out on a large scale. In one plant,[4] operated at Toronto, Canada, from May 1916 to November 1918, more htan 6,000,000 lbs. of acetone and 12,000,000 lbs. of alcohol were obtained. The breaking down of carbohydrates into acetone can be effected by the use of *Bacillus granulobacter pectinovorum,*[1] *Bacillus macerans,*[2] *Bacillus acetoethylicum,*[3] and no doubt by other types of bacteria.

Aside from securing the proper organism and proper conditions for fermentation, an essential requirement is a cheap source of fermentable carbohydrate. The chief materials fermented have been corn meal and molasses. As a cheap substitute for these materials, the utilization of wood waste, straw, seed hulls, and corncobs is suggested.

In a recent paper[7] the authors have described the results obtained by fermenting crude corncob sirup with the pentose fermenter, *Lactobacillus pentoaceticus.* The results obtained indicate that a sirup prepared by the hydrolysis of corncobs with dilute acids offers a favorable medium for the fermentative action of these bacteria. In the present paper are given the results obtained by fermenting a similar corncob sirup with another organism, *Bacillus acetoethylicum,* whose isolation, fermentation characteristics, and commercial use have been described by Northrop and his associates. A more detailed description of the products of fermentation and conditions influencing these products was given in a later paper by Arzberger, Peterson, and Fred.[8]

The chief products formed by this organism are acetone, ethyl alcohol, formic and acetic acids, and carbon dioxide. The biochemical relations of these products to one another are very intimate, as may be seen from the fact that a high production of acetone and alcohol is accompanied by a low yield of volatile acids. Conversely, when the acid production is high, the acetone and alcohol yields are low. The condition determining this variation of the products is the reaction of the medium. An alkaline reaction, pH 8.0, favors the production of acid, while an acid reaction of pH 5 to 7 increases the yield of acetone and alcohol.

HYDROLYSIS OF CORNCOBS

A dilute sugar solution was prepared by hydrolyzing ground corncobs with sulfuric acid. After hydrolysis, the acid was neutralized with milk of lime, and the sugars were removed by pressing and washing the insoluble residue. The production of reducing sugars is influenced by the quantity of acid, the volume of water, the length of heating, and the pressure maintained during the hydrolysis. At a pressure of 20 lbs. the most efficient production of sugars was effected by heating the cobs for 1 hr. with about 8 per cent of their weight of acid. A greater quantity of acid and water increased the yield only 2 per cent. At a pressure of 100 to 115 lbs., with 2 per cent of acid, somewhat lower yields of sugar were obtained. A second hydrolysis of the residue gave only 4.4 per cent of reducing sugars. The percentages of sugar obtained and other data for the different methods of hydrolysis are given in Table I.

FERMENTATION OF PRODUCTS OF HYDROLYSIS

PRELIMINARY TESTS—To determine the fermentability ot the corncob sugars, test tube cultures containing 3.0 per cent of reducing sugar, 0.5 per cent of peptone, and 0.1 per cent of solid Na_2HPO_4 (approximately $2H_2O$) were prepared. Varying amounts of sterilized sodium hydroxide were added, so that the pH value of the medium in the tubes ranged from 6.4 to 8.8. After a few days the unfermented sugar was determined, and it was found that the greatest fermentation had taken place where the pH was between 7.6 and 8.4 at the time of inoculation.

FERMENTATION SERIES, I—The effect of extracting the cobs with alkali on the fermentability of the hydrolysis products was studied in this experiment. Convenient portions of Solutions 2, 5, and 7 (Table I) were used. The solutions were placed in 500-cc. Erlenmeyer flasks, together with sufficient peptone and Na_2HPO_4 to give a concentration of 0.5 and 0.1 per cent, respectively. The flasks were stoppered with cotton plugs and sterilized for 30 min. at 15 lbs. pressure. When cold, an excess of sterilized calcium carbonate was added to the flasks, and the pH of the medium was adjusted to 7.6 to 8.0 by the addition of sterilized sodium hydroxide.[1] The flasks of media were inoculated, and the cotton plugs were covered with tin foil to prevent the loss of alcohol and acetone.

Considerable difficulty was experienced at first in securing growth in these cultures. Sugar determinations showed that little or no reducing sugars had been fermented. The

---

1 Received April 27, 1921.

2 This work was in part supported by a grant from the special research fund of the University of Wisconsin.

3 Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

4 H. B. Speakman, *J. Biol. Chem.*, **41** (1920), 319

5 F. Schardinger, *Centr. Bakt. Parasitenk. I., II Abt.*, **14** (1905), 772.

6 J. H. Northrop, L. H. Ashe, and J. K. Senior, *J. Biol. Chem.*, **39** (1919), 1; J. H. Northrop, L. H. Ashe, and R. R. Morgan, THIS JOURNAL, **11** (1919), 723.

7 E. B. Fred and W. H. Peterson, THIS JOURNAL, **13** (1921), 211.

8 *J. Biol. Chem.*, **44** (1920), 465.

[1] In some earlier experiments, the pH was adjusted before the medium was sterilized, but it was found that the solution had become acid asa result of sterilizatson, and that from 15 to 20 per cent of the reducing sugars had been destroyed.

TABLE I—REDUCING SUGARS OBTAINED FROM CORNCOBS BY VARIOUS METHODS OF HYDROLYSIS

No.	Material	G.	Reagent	C.	Volume of Water Cc.	Heating Time Min.	Heating Press. Lbs.	Reducing Sugars as Glucose Per cent[1]
1	Cobs	50	H_2SO_4	4	200	60	20	24.5
2	Cobs	200	H_2SO_4	30	1500	120	20	26.7
3	Cobs	20	H_2SO_4	1.6	80	240	20	31.4
4	Cobs	100	NaOH	30	1000	120	20	10.0
5	Residue from 4		H_2SO_4	20	1000	120	20	9.1
6	Cobs	50	NaOH	2	500	15	20	2.8
7	Residue from 6		H_2SO_4	10	500	120	20	21.9
8	Cobs	100	H_2SO_4	2	200	30	100-115	20.7
9	Residue from 8		H_2SO_4	2	200	20	100-115	4.4

[1] Air dry cobs.

cultures had become acid in reaction and growth had apparently ceased. More Na_2HPO_4 was added, the pH was adjusted with sodium hydroxide, and the flasks were reinoculated. After a few days the cultures were tested for acetone, and good qualitative tests were obtained. Microscopic mounts of the cultures showed the presence of large numbers of bacteria. At the end of 10 days sugar determinations were made, and it was found that about one-half of the reducing sugars had been fermented. The cultures were analyzed for acetone, alcohol, and volatile acids.

Methods of Analysis—The acetone and alcohol were distilled from a 50-cc. portion of the culture, which had been previously neutralized with sodium hydroxide and saturated with sodium chloride in order to hasten the removal of the acetone and alcohol. An aliquot part of the distillate was used for the determination of acetone, according to Goodwin's modification[1] of the Messinger-Huppert method. In another aliquot part the alcohol was oxidized with potassium dichromate, and the resulting acids were removed by distillation and titrated.[2]

A second portion of the culture was acidified with sulfuric acid, and the volatile acids were driven out by steam distillation and titrated.

TABLE II—ACETONE FERMENTATION OF THE HYDROLYSIS PRODUCTS OF CORNCOBS
(Calculated for 100 cc. of culture)

No. of Corncob Extract	Age of Culture Days	Reducing Sugar as Glucose G.	Acetone G.	Alcohol as Ethyl Gl.	Volatile Acids as Acetic G.	Sum of Products G.	Sugar Ferm. G.
Table I, No 2........	10	5.02	0.320	0.854	0.636	1.810	2.73
Table I, No 5........	7	4.02	0.139	0.266	0.286	0.691	1.39
Table I, No. 7........	8	3.60	0.083	0.233	0.281	0.597	1.94

From the analytical data which are given in Table II, it is evident that the optimum conditions for the growth of the bacteria were not obtained. Unfavorable reaction and the tendency of the bacteria to mat together as a slime on the bottom of the flask were probably responsible.

FERMENTATION SERIES, II—The distribution of the bacteria is maintained much better if the flask is filled with some coarse, inert material to which the organisms may attach themselves. Northrop, Ashe, and Morgan[3] suggested use of broken corncobs, coke, or beech shavings. In this experiment a liter Jena bottle was two-thirds filled with coarse cinders, which were extracted with 10 per cent hydrochloric acid and washed free of acid. The bottle was closed with a 2-hole rubber stopper through which were inserted glass tubes somewhat similar to those used in an ordinary wash bottle. Instead of the short tip on a wash bottle a long glass tube was used, and a guard tube filled with cotton was attached to the second tube, which corresponded to the mouth piece of a wash bottle. During the fermentation the delivery tube was closed by a screw clamp, while the guard tube was left open as a means of escape for the fermentation gases. A sample for analysis was removed when desired by attaching a rubber force bulb to the guard tube, pumping air into the flask, and then opening the screw clamp. The first 10 cc. coming out was always discarded. When sufficient sample had been collected the screw clamp was closed, the force bulb was disconnected, and the air pressure in the flask was released through the guard tube. At the end of the fermentation all the liquid in the bottle was forced out, leaving the bacterial slime attached to the cinders. The bottle was again charged with 400 to 500 cc. of medium by sucking this into the bottle through the delivery tube. With this arrangement a rapid and continuous fermentation was maintained, the yield of products was much increased, and the time of fermentation considerably shortened. One experiment with one refill and two e periments with two renewals each were made. The results of the analyses are given in Table III. The most rapid fermentation took place in the second refill of Expt. I. In 6 days, 2.114 g. of products were obtained from the fermentation of 2.82 g. of sugar. The maximum yields of acetone and alcohol were found in this case, while the volatile acid was correspondingly low. The relation of these three products to one another and to the sugar consumed may be more clearly seen by a recalculation on a percentage basis, as has been done in Table IV. The figures previously reported for the fermentation of the pure carbohydrates by *Bacillus acetoethylicum* are included in this table for comparison. More acetone and alcohol and less volatile acids were obtained from the fermentation of the corncob extract than had been found in the fermentation of the pure carbohydrates. In both experiments the second charge shows an increase over the first in the proportion of acetone and alcohol. These two products are characteristic of the later stages of the fermentation, and hence a method of fermentation which leaves the bacteria in the container and renews the sugar favors the formation of acetone and alcohol.

TABLE III YIELD OF PRODUCTS BY A CONTINUOUS FERMENTATION
(Calculated for 100 cc. of culture)

Expt.	No. of Refill	Age of Culture Days	Reducing Sugars Glucose G.	as Acetone G.	Alcohol as Ethyl G.	Volatile Acid as Acetic G.	Total Products G.
I.....	1	0	2.23	.....	.....	.....	.....
		4	0.77	0.197	.....	.....	.....
		9	0.22	0.342	0.681	0.295	1.318
I.....	2	0	3.28	.....	.....	.....	.....
		3	1.84	0.390	0.570	.....	.....
		6	0.46	0.502	1.051	0.561	2.114
II.....	1	0	3.63	.....	.....	.....	.....
		6	0.35	0.306	0.970	0.409	1.685
II.	2	0	3.42	.....	.....	.....	.....
		4	1.00	0.309	0.810	0.408	1.527
		8	0.42	0.381	1.047	0.377	1.805
III.....	1	0	3.15	.....	.....	.....	.....
...		6	0.28	0.206	0.670	0.372	1.248

TABLE IV—PERCENTAGE OF PRODUCTS ON THE BASIS OF SUGAR FERMENTED

Expt	No. of Refill	Acetone Per cent	Alcohol Per cent	Volatile Acid Per cent	Total Per cent
I.	1	16.1	32.1	13.9	62.1
I.	2	17.8	37.3	20.0	75.0
II.....	1	9.3	30.0	15.5	54.8
II..	2	12.7	34.9	12.6	60.2
III..	1	7.2	23.3	13.0	43.5
AVERAGE		12.6	31.5	15.0	59.1
Average for 10 fermentations of purmentations of purified carbohydrates[1]		8.7	25.5	21.7	55.6

[1] *Loc. cit.*

From the data of Tables I to III the yield of products may be expressed on the basis of 100 lbs. of corncobs. An average of 25 lbs. of reducing sugars were formed, and of this 90 per cent, or 22.5 lbs., were fermented, yielding about 2.7 lbs. of acetone, 6.8 lbs. of alcohol, and 3.4 lbs. of volatile acids.

---

[3] *J. Am. Chem. Soc.*, **42** (1920), 39.

[2] A. W. Dox and A. R. Lamb, *J. Am. Chem. Soc.*, **38** (1916), 2561.

[1] *Loc. cit.*

Summary

Corncobs may be utilized for the production of acetone, ethyl alcohol, formic acid, and acetic acid. These products may be obtained by fermenting a sirup which is made from corncobs by hydrolysis with dilute sulfuric acid. This hydrolysis is easily brought about and, based on the weight of corncobs, yields from 25 to 30 per cent of reducing sugars, mainly xylose.

This crude xylose sirup is readily and almost completely fermented by *Bacillus acetoethylicum* with the production of the above products. On the basis of 100 lbs. of corncobs, the yield of products is 2.7 lbs. of acetone, 6.8 lbs. of alcohol, and 3.4 lbs. of volatile acids.

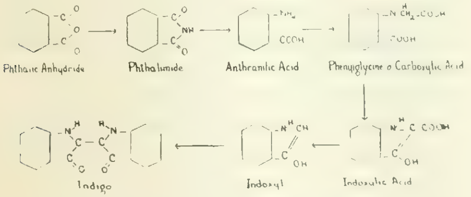
The best results are obtained by conducting the fermentation in a container partly filled with cinders. The bacteria become attached to these cinders, thus bringing about a good distribution of cells throughout the culture. At the end of the fermentation the solution is removed, and a fresh charge is added without disturbing the bacterial slime. An immediate and vigorous fermentation ensues. An important condition that must be observed is the reaction of the medium. This should be between pH 7.6 and 8.4 at the beginning of the fermentation, and an abundance of calcium carbonate should be present to neutralize the acids that are formed.

Alkali Fusions. III—Fusion of Phenylglycine-*o*-Carboxylic Acid for the Production of Indigo[1]

By Max Phillips

Color Laboratory, Bureau of Chemistry, Deaprtment of Agriculture, Washington, D. C.

The Gibbs and Conover[2] catalytic process for making phthalic anhydride, developed in this laboratory, has already assumed considerable industrial importance, and phthalic anhydride promises to become one of the cheapest intermediates. Of the many dyes that can be made from this compound, by far the most important one is unquestionably indigo. A process of making this dye from phthalic anhydride has been used by the Badische company for nearly twenty-five years. The various steps involved in the so-called Badische process may be represented as follows:



Although the chemistry involved in this process is now very generally known, the details for carrying it out have never, for obvious reasons, been published by the Badische company. A study of the various steps involved in this process has, therefore, been undertaken in this laboratory, and the present article is a report of one phase of the work.

Historical Review

The process of making indigo from phenylglycine-*o*-carbolic acid was first brought to the attention of chemists by Heumann[3] in 1890, and subsequently patented by the Badische company. According to Heumann, three parts of potassium hydroxide, one part phenylglycine-*o*-carboxylic acid, and one part of water are heated to 180° to 200° C. until the alkaline mass assumes an intense orange color, whereupon it is allowed to cool and subsequently dissolved in water, and the indigo is precipitated by passing a stream of air through the solution. The yield obtained is not given. The Badische[4] patent controlling this process fails to give any further information. In a later patent[5] it is claimed that the heating of the phenylglycine-*o*-carboxylic acid must be done in the absence of air or in an atmosphere of an inert gas. Using sodium hydroxide, a temperature range of 235° to 265° C. is given, whereas with potassium hydroxide that of 280° to 290° C. is recommended. It is also claimed that the alkali used must be as dry as possible.

According to Levinstein,[1] the conversion of phenyglycine-*o*-carboxylic acid to indoxylic acid is accomplished by heating a mixture consisting of 60 parts phenylglycine-*o*-carboxylic acid and 100 parts of sodium hyroxide for 2.75 hrs. at 260° C. No statement as to yield is given.

In a patent granted to Michel[2] it is claimed that the addition of paraffin to the alkali fusion mixture greatly improves the yield of indigo. The fusion temperature range is given as from 250° to 280° C. The end of the reaction is determined by the color of the fused mass. However, it does not appear that this method has ever found any practical application.

Materials and Apparatus

POTASSIUM HYDROXIDE AND SODIUM HYDROXIDE—These chemicals were of the usual C. P. grade. The potassium hydroxide assayed 81.2 per cent KOH, and the sodium hydroxide 94.0 per cent of NaOH. In calculating the moles of alkali used in the various fusion experiments, due allowance was made for the impurities present.

PHENYGLYCINE-*o*-CARBOXYLIC ACID—This acid was prepared by condensing anthranilic acid with chloroacetic acid. In preparing it by this method it is usually recommended that sodium hydroxide or sodium carbonate be used as the condensing agent. It was found, however, that a purer product could be obtained if these were eliminated. The following is a brief description of the method used: 137 g. anthranilic acid (1 mole), 94.5 g. chloroacetic acid (1 mole), and 1000 cc. of water were placed in a suitable flask attached to a reflux condenser and heated for about 3 hrs. On cooling, crystals of phenylglycine-*o*-carboxylic acid separated out. These were filtered off and recrystallized from hot water. About 1000 g. of this acid were prepared, and the same material was used in all of the experiments recorded in this paper. A nitrogen determination made on this acid gave the following results:

Found Per cent N	Calculated for $C_9H_9O_4N$ Per cent N
7.13	7.18
7.18	

APPARATUS—A full description of the apparatus used will be found in an earlier article.[3]

---

[1] Received June 20, 1921.

[2] U. S. Patents 1,284,888 and 1,285,117; This Journal, 11 (1919), 1031.

[3] *Ber.*, 23 (1890), 3431.

[4] D. R. P. 56,273.

[5] D. R. P. 85,071.

[1] *J. Soc. Dyers Colour.*, 17 (1901), 138.

[2] *Chem. Ztg.*, 35 (1911), 735; D. R. P. 232,986.

[3] This Journal, 12 (1920), 145.

EXPERIMENTAL METHODS

In working out the most favorable conditions for the conversion of phenylglycine-*o*-carboxylic acid to indoxylic acid and hence to indigo, a study was made of the four following factors affecting the yield of indigo:

1—The proper fusion period.
2—Ratio of alkali to phenylglycine-*o*-carboxylic acid.
3—The proper fusion temperature.
4—The proper condensing agent.

With the apparatus used the effect upon the yield of indigo of each of the above factors could be very conveniently studied. Thus, to determine the optimum fusion period, with potassium hydroxide as the condensing agent, experiments were performed in which the period of fusion was the only variable factor, while the temperature, as well as the ratio of phenylglycine-*o*-carboxylic acid to potassium hydroxide, remained constant. From the results thus obtained, the optimum fusion period with reference to the other experimental conditions was deduced. Using the optimum conditions as determined in the preceding set of experiments, and again keeping the temperature constant, experiments were performed in which the ratio of phenylglycine-*o*-carboxylic acid to potassium hydroxide varied. At the end of the fusion period, the tubes were rapidly cooled and their indigo content determined. To determine the optimum fusion temperature, experiments were performed at different temperatures, using the optimum conditions as to period of fusion and ratio of phenylglycine-*o*-carboxylic acid already determined. In a similar manner the conversion of phenylglycine-*o*-carboxylic acid to indigo by means of sodium hydroxide, as well as with various mixtures of potassium hydroxide and sodium hydroxide, were studied.

INDIGO DETERMINATION—The cold alkaline mass was dissolved in hot water and the solution gently boiled for about half an hour. Air was then slowly passed through the solution until no more indigo separated out. This usually required about 8 to 10 hrs. The indigo was collected on a weighed hardened filter paper, and washed with hot dilute hydrochloric acid, then with hot water, and finally with alcohol and ether. It was dried at 110°C. and its weight determined. The result thus obtained is given in the following tables under the heading "Indigo Obtained—Grams." The purity of the indigo was determined by means of the Rawson[1] potassium permanganate method. This method is unquestionably as accurate as any of the methods for the determination of indigotin and by far the simplest.[2] The potassium permanganate solution was standardized against pure indigo prepared according to the Badische[3] method. In sulfonating the pure indigo, the directions given by Rawson in connection with his method for determining indigotin were followed so as to make the results comparable. The weight of pure indigo found was calculated as per cent of the theory.

EXPERIMENTS WITH POTASSIUM HYDROXIDE

EFFECT OF TIME OF FUSION ON INDIGO YIELD—The results of several experiments in which the time of fusion was made the only variable factor, while the temperature and ratio of phenylglycine-*o*-carboxylic acid to potassium hydroxide remained constant, are given in Table I and shown graphically in Fig. 1.[4]

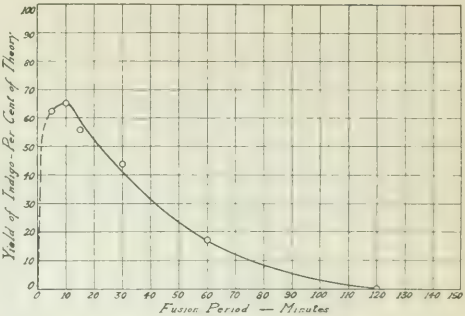


FIG. 1—FUSION PERIOD-YIELD CURVE
(Ratio of $C_6H_4(COOH)NH.CH_2.COOH$: KOH = 1 : 8. Temperature, 270° C.)

TABLE I—EFFECT OF VARYING FUSION PERIOD
Ratio $C_6H_4(COOH)NH.CH_2.COOH$: KOH = 1:8 (0.05 mole, 0.4 mole).
Fusion temperature 270°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1..........	5	4.1415	99.02	62.7
2..........	10	4.3320	99.0	65.3
3..........	15	4.2980	85.2	55.9
4..........	30	3.7530	76.6	43.8
5..........	60	2.0358	46.1	17.4
6..........	120	0.0000	00.0	00.0

This table indicates that the maximum yield of indigo was obtained when the fusion was conducted for 10 min. It appears that the reaction between potassium hydroxide and phenylglycine-*o*-carboxylic acid proceeds quite rapidly, so that a longer fusion period is not only unnecessary, but is actually detrimental so far as the yield of indigo is concerned. In the subsequent experiments, therefore, the optimum fusion period of 10 min. was used.

EFFECT OF AMOUNT OF POTASSIUM HYDROXIDE UPON THE YIELD OF INDIGO—The results of fusion experiments using different amounts of potassium hydroxide, but keeping the temperature and time of fusion constant, are recorded in Table II and graphically in Fig. 2 (Curve *a*).

TABLE II—EFFECT OF VARYING AMOUNT OF POTASSIUM HYDROXIDE
9.75 g. (0.05 mole) $C_6H_4(COOH)NH.CH_2.COOH$ used in each experiment
Fusion temperature 270°C. Period of fusion 10 min.

No.	Moles KOH	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1..........	4	0	0	0
2..........	6	2.7816	61.7	26.2
3..........	10	5.0905	96.5	75.0
4..........	12	5.3695	99.6	81.6
5..........	14	5.6893	98.4	85.4
6..........	16	5.9396	95.8	86.8
7..........	20	5.9426	96.1	87.2

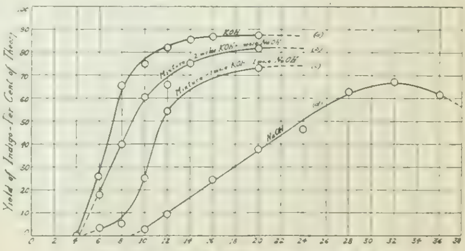


FIG. 2—CONCENTRATION-YIELD CURVES

The results show that the yield of indigo increases at first rather rapidly with the increase in concentration of the potassium hydroxide until it reaches a maximum. Although the highest yield of indigo was obtained when 20 moles potassium hydroxide to 1 mole of phenylglycine-*o*-carboxylic acid were used, it is nevertheless apparent that practically the same yield was obtained when the molar ratio of potassium hydroxide to phenylglycine-*o*-carboxylic acid was 16:1, the difference between the two results being so small as hardly to warrant the use of the higher concentration of potassium hydroxide. In the following series of experiments, 16 moles of potassium hydroxide to 1 mole of phenylglycine-*o*-carboxylic acid were, therefore, used.

---

[1] *Chem. News*, 51 (1885), 255.

[2] A good review of the various methods for the determination of indigotin is given by Bergtherl and Briggs, *J. Soc. Chem. Ind.*, **25** (1906), 729.

[3] *Z. Farben-Ind.*, 8 (1909), 121.

[4] The curves given in this article were drawn by Mr. G. H. Mains of this laboratory.

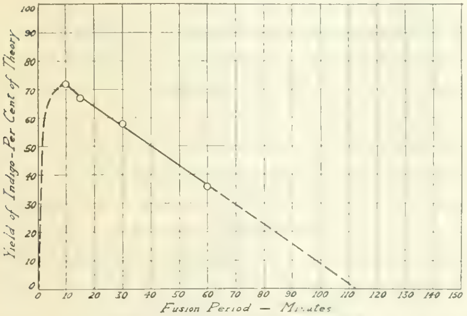


FIG. 3—FUSION PERIOD YIELD CURVE
(Ratio of C_6H_4(COOH)NH.CH$_2$.COOH : KOH = 1 : 16. Temperature, 200° C.)

EFFECT OF TIME OF FUSION ON INDIGO YIELD, 2ND SERIES—Inasmuch as the previous determinations of the optimum fusion period were carried out under rather unfavorable conditions, more especially as regards the concentration of potassium hydroxide (see Table 1), it seemed, therefore, desirable to repeat these experiments using, however, the optimum concentration of potassium hydroxide. The results of these experiments are shown in Table III, and graphically in Fig. 3.

TABLE III—EFFECT OF VARYING FUSION PERIOD (2ND SERIES)
Ratio of C_6H_4(COOH)NH.CH$_2$COOH : KOH = 1:16 (0.05 mole:0.8 mole).
Fusion temperature 290°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	10	5.0096	93.9	71.8
2..........	15	4.7240	92.7	66.8
3	30	4.2240	90.0	58.0
4..	60	2.7044	86.9	35.8

On comparing the results given in Tables I and III, it will be observed that in either case the maximum yield of indigo was obtained when the fusion was conducted for only 10 min. This optimum fusion period was, therefore, used in the subsequent fusion experiments with potassium hydroxide.

EFFECT OF THE TEMPERATURE OF FUSION ON YIELD OF INDIGO—The results of fusion experiments at temperatures of 240°, 260°, 270°, 290°, and 300°C. are recorded in Table IV and graphically in Fig. 4 (Curve *a*).

TABLE IV—EFFECT OF VARYING TEMPERATURE
Ratio of C_6H_4(COOH)NH.CH$_2$COOH : KOH = 1 : 16 (0.05 mole : 0.8 mole).
Fusion period 10 min.

No.	Temp. of Fusion °C.	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1......	240	4.6726	99.4	70.9
2..........	260	6.1234	95.4	89.1
3..........	270	5.9396	95.8	86.8
4....	290	5.0096	93.9	71.8
5..........	300	4.1872	91.2	58.8

It appears from these results that 260°C. is the optimum temperature for the conversion of phenylglycine-*o*-carboxylic acid into indigo. At higher temperatures some of the indoxylic acid formed is destroyed, so that a somewhat reduced yield of indigo is obtained.

EXPERIMENTS WITH SODIUM HYDROXIDE

EFFECT OF TIME OF FUSION ON INDIGO YIELD—The results of experiments in which the time of heating was made the only variable factor are given in Table V.

TABLE V—EFFECT OF VARYING FUSION PERIOD
Ratio of C_6H_4COOH.NH.CH$_2$.COOH : NaOH = 1 : (0.05 mole : 0.8 mole).
Temperature 270°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	5	0	.	.
2	15	1.1940	80.3	14.6
3	30	0	.	.
4	60	0	.	.

It will be observed that indigo was obtained only in Expt. 2. Temporarily adopting 15 min. as the optimum period and using this as a basis for further study, experiments were performed in which the concentration of sodium hydroxide was the only variable factor. The results obtained are given in Table VI and graphically in Fig. 2 (Curve *d*).

TABLE VI—EFFECT OF VARYING AMOUNT OF SODIUM HYDROXIDE
9.75 g. C_6H_4(COOH)NH.CH$_2$.COOH (0.05 mole used in each experiment).
Fusion temperature 270°C. Period of fusion 15 min.

No.	Moles NaOH	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1... .	10	0.2171	82.9	2.7
2	12	0.6506	94.5	9.4
3........	16	1.7763	91.2	24.7
4... ...	20	2.6852	91.9	37.7
5 .. .	24	3.2015	95.9	46.9
6.	28	4.3519	94.9	63.0
7..........	32	4.7183	93.4	67.3
8	36	4.3339	93.1	61.6

In connection with these results, it will be observed that within certain limits the yield of indigo increases with the increase in the concentration of the sodium hydroxide, the maximum yield being obtained when the molar ratio of phenylglycine-*o*-carboxylic acid to sodium hydroxide is 1:32. This increase in the yield of indigo with the increase in the concentration of alkali was also found to be true in the case of potassium hydroxide (see Table II and Fig. 2, Curve *a*). With sodium hydroxide, however, the conversion of phenylglycine-*o*-carboxylic acid proceeds much more slowly than with potassium hydroxide under similar conditions. Although it may appear that a much higher molar concentration of sodium hydroxide than potassium hydroxide is necessary to get the maximum yield of indigo, nevertheless, weight for weight, the difference is not very great, more especially as ordinary C. P. potassium hydroxide usually assays about 80 per cent KOH, whereas

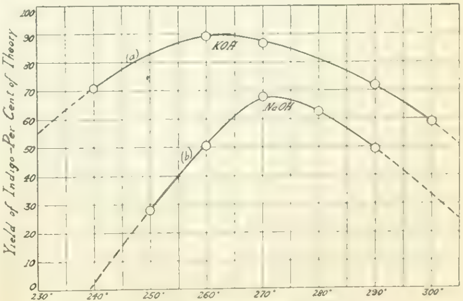


FIG. 4—FUSION TEMPERATURE YIELD CURVES

an ordinary sodium hydroxide will assay about 95 per cent NaOH.

EFFECT OF THE TEMPERATURE ON THE YIELD OF INDIGO—Using the optimum concentration of sodium hydroxide already determined and keeping the time constant, experiments were performed at different temperatures. The results obtained are tabulated in Table VII and shown graphically in Fig. 4 (Curve *b*).

TABLE VII—EFFECT OF VARYING TEMPERATURE

Ratio of $C_6H_4(COOH)NH.CH_2.COOH$: NaOH = 1 : 32 (0.05 mole : 1.6 moles). Time, 15 min.

No.	Fusion Temperature °C.	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1..........	250	1.9329	94.3	27.8
2..........	260	3.3997	97.0	50.3
3..........	270	4.7183	93.4	67.3
4..........	280	4.4239	92.5	62.5
5..........	290	3.6888	88.0	49.5

From these results it appears that 270°C. is the optimum temperature for the preparation of indigo from phenylglycine-*o*-carboxylic acid and sodium hydroxide.

DETERMINATION OF THE OPTIMUM TIME—Inasmuch as the experiments already made in this connection were of rather a preliminary nature (Table V), several additional experiments were performed under more favorable experimental conditions, more especially as regards temperature and concentration of sodium hydroxide. The results of these experiments are given in Table VIII and graphically in Fig. 5.

TABLE VIII—EFFECT OF VARYING TIME OF THE REACTION

Ratio of $C_6H_4(COOH)NH.CH_2.COOH$: NaOH = 1 : 32 (0.05 mole : 1.6 moles). Temperature, 270°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1..........	10	4.0416	95.5	58.9
2	15	4 7183	93 4	67 3
3..........	30	5.5022	82.5	69.3
4..........	60	4.8816	85 9	64 0
5..........	120	2.7649	86.8	36.6
6..........	150	2.4566	84.9	31.8

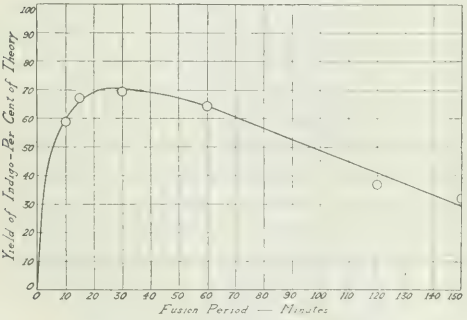


FIG. 5—FUSION PERIOD-YIELD CURVE
(Ratio of $C_6H_4(COOH)NH.CH_2.COOH$: NaOH = 1 : 32 Temperature, 270° C.)

From these results it can be seen that the maximum yield of indigo was obtained when the experiment was conducted for 30 min. A longer period was not only unnecessary but quite undesirable.

Inasmuch as the results obtained seemed to be at variance with those of Levinstein,[1] several experiments were carried out following the procedure suggested by Levinstein. However, all of the experiments gave negative results, no indigo at all being obtained. This result was to be expected, considering the low proportion of sodium hydroxide to the phenylglycine-*o*-carboxylic acid and the long heating period (See Tables VI, VIII, Fig. 2, Curve *d*, and Fig. 5).

EXPERIMENTS WITH MIXTURES OF POTASSIUM AND SODIUM HYDROXIDES

In view of the fact that somewhat better yields of indigo were obtained with potassium hydroxide than with sodium hydroxide, experiments were carried out with different mixtures of these two alkalies, in the hope of getting higher yields of indigo than were obtained with the pure alkalies. The results of two series of experiments utilizing two different mixtures of potassium and sodium hydroxides are given in Table IX, and are illustrated graphically in Fig. 2, Curves *b* and *c*.

TABLE IX—EFFECT OF VARYING AMOUNT OF ALKALI MIXTURE

9.75 g. (0.05 mole) of $C_6H_4(COOH).NH.CH_2.COOH$ were used in each experiment. Fusion temperature, 270°C. Period of fusion, 10 min.

No.	Moles of Alkali Mixture	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
		2 KOH : 1 NaOH		
1..........	6	2.6684	44.2	18.0
2..........	8	2.8620	91.5	39.9
3..........	10	4.2516	93.6	60.8
4..........	12	4.4625	96.6	65.9
5..........	14	5.1433	96.3	75.6
6..........	20	5.5912	95.7	81.6
		1 KOH : 1 NaOH		
1..........	6	0.6547	34.2	3.4
2..........	8	1.5867	22.1	5.3
3..........	10	3.5805	46.4	25.3
4..........	12	4.6374	76.3	54.0
5	20	4.8853	98.4	73.3

It will be noted from the results given in these tables that, while the aim was not entirely realized, nevertheless much better yields were obtained than with sodium hydroxide alone under similar conditions. However, inasmuch as the results indicated that the yield of indigo obtained is a function of the quantity of potassium hydroxide present in the alkali mixture, no further experiments were carried out along this line.

SUMMARY

A study of the fusion of phenylglycine-*o*-carboxylic acid with potassium hydroxide, sodium hydroxide, and various mixtures of these two alkalies has been made, and the optimum conditions for carrying out this reaction have been determined.

The results of the experiments with potassium hydroxide as the condensing agent indicate that 260°C. is the optimum fusion temperature, 10 min. the optimum fusion period, and 12 to 16 moles potassium hydroxide to 1 mole phenylglycine-*o*-carboxylic acid, the optimum fusion mixture.

Using sodium hydroxide as the condensing agent, 270°C. has been found to be the optimum temperature, 25 to 30 min. the optimum time, and 28 to 32 moles sodium hydroxide to 1 mole phenylglycine-*o*-carboxylic acid the optimum mixture.

Potassium hydroxide has been found to give higher yields of indigo than sodium hydroxide.

Mixtures of these two alkalies give better yields of indigo than sodium hydroxide alone, the yield increasing with the increase of the ratio of potassium hydroxide with respect to the sodium hydroxide.

The zinc dust produced in the United States in 1920, as reported to the U. S. Geological Survey by 12 plants, showed an increase in 1920 as compared with 1919 of over 70 per cent, in both quantity and value.

ZINC DUST PRODUCED IN 1919-1920

	Quantity Short Tons	Value Based on Sales	Average Price per Lbs Cents
		1919	
Prepared "blue powder"......	4,083	$801,366	9.8
"Atomized" zinc dust........	2,515	524,694	10.4
		1920	
Prepared "blue powder"......	9,066	$2,009,117	11.1
"Atomized" zinc dust........	2,273	512,833	11.3

---

[1] *Loc. cit.*

The Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese[1, 2]

By Robert E. Wilson, W. Grenville Horsch, and Merrill A. Youtz

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

This paper deals with the formation of permanganates by the electrolytic method, in which bars of ferromanganese serve as anodes in a solution of sodium or potassium carbonate or hydroxide. The manganese is oxidized to the heptavalent state, forming permanganate directly in solution.

The experiments herein recorded owe their origin to the demand which arose during the war for a very pure grade of sodium permanganate. Of the possible methods of producing sodium permanganate, this electrolytic method undoubtedly is the one best adapted to yield the chemically pure salt directly, since the only soluble contaminating substance is carbonate (or hydroxide) and this is destroyed in the course of the electrolysis, which may even be carried to the point of forming permanganic acid. This is an important consideration in view of the difficulty of purifying sodium permanganate made by the customary chemical methods.

A brief summary of the investigations carried out by the authors during the war has already been published.[3] Since then, the authors have been interested to extend the study of this process in two respects—first, to study further the production of sodium permanganate in order to determine the optimum conditions more precisely and, if possible, to eliminate certain difficulties in its technical application, and, second, to make a careful comparative study of the process as applied to the production of potassium permanganate. Incidentally, many of the previous sodium permanganate experiments have been repeated in order that directly comparable results might be obtained with the same anodes. Both carbonate and hydroxide solutions were used as anolytes. A total of more than one hundred and eighty carefully controlled runs were made, each run having a duration, on the average, of 5 hrs. A few runs were made which lasted continuously from 7 to 10 days.

Very little work has been published on the production of permanganates electrolytically from ferromanganese. A bibliography up to 1919 is given in an article by Thompson,[4] who produced potassium permanganate in a 350-amp. cell which showed a current efficiency in K_2CO_3 anolyte of about 17 per cent at 40°. A higher efficiency would have been obtained with better diaphragms. The anodes used by Thompson contained 75 per cent Mn, 16.7 per cent Fe, 6.1 per cent C, and small amounts of Si and P, and did not show passivity under the conditions mentioned. At temperatures much above 40°, an insulating coating of oxides formed which prevented the production of permanganate. Thompson believes that the anodic behavior, as regards formation of insulating scale, is affected by small changes in the relative amounts of iron and manganese in the anode.

While this manuscript was being prepared for publication, an article by Henke and Brown[5] appeared. These authors worked with hydroxide electrolytes exclusively, and their experiments differed from those by the present authors in that no diaphragm was used and calcium hydroxide was added to the sodium hydroxide electrolyte. The calcium hydroxide apparently formed a film over the platinum cathode which acted as a diaphragm. Their experiments showed that the current efficiency increases with the current density and diminishes with rising temperature, and that the curve of current efficiency against base concentration has a decided minimum.

APPARATUS

Except as otherwise noted, the electrolyses were carried out in a cell which consisted of a cylindrical glass jar (12.5 cm. in diameter by 15 cm. high), containing within it a porous porcelain cup (5 cm. in diameter by 12.5 cm. high) which served as a diaphragm. In this cell were placed the two electrodes, the cathode (of 16-gage sheet iron, 3 cm. by 15 cm.) being within the cup, and the ferromanganese anode standing in the jar outside, and about 3 cm. away from the cup. The freshly cast anodes had the dimensions 2.5 cm. square by 15 cm. in height. Electrical contact with the anode was made by clamping a strip of brass, carrying a binding post, against a freshly ground surface near the top.

Several cells (usually six) were operated simultaneously, being connected in series across a source of direct current. The circuit also contained an ammeter, a copper coulometer, and a rheostat. Provision was made for connecting a voltmeter across any individual cell. Readings of these several instruments furnished the electrical data.

The temperature of each cell was determined by reading a mercurial thermometer placed in the anolyte not far from the anode. In most of the experiments the temperature was controlled by placing the whole row of cells in a long water bath maintained at a temperature somewhat below that desired within the cells, and by inserting in each anolyte a cooling coil made of glass, the flow of water through which could be adjusted to compensate for irregular heating in any particular cell.

PROCEDURE

A typical electrolytic run was conducted in the following manner: Each of the cells of a series was filled with anolyte, the porous cups filled with catholyte and placed in the respective cells, the electrodes inserted, and electrical connections made. This was done as rapidly as possible, and the circuit was closed immediately afterward in order to avoid inter-diffusion of anolyte and catholyte, which usually differed from each other in composition. During the run, the electrolyte was stirred occasionally, and the temperature was observed immediately thereafter. The flow of cooling water was adjusted to keep the temperature constant within 3° or 4°C. The current was kept constant throughout the run to within about 1 per cent. The usual length of run was 5 hrs. At the conclusion of the electrolysis the anodes, cooling coils, and porous cups were removed, and the adhering anolyte was washed into the main solution with distilled water. The catholyte always was discarded, and care was taken to avoid getting any of it into the anolyte.

In cases where the "material" efficiency of the anode was to be determined, the weights of the anode before and after the run were obtained. To insure uniform conditions, the anode was treated after each electrolysis with a 2 per cent solution of acetic acid containing sufficient hydrogen peroxide to cause the rapid removal of the manganese dioxide coating. The anodes were kept in this solution just long enough to give a clean, metallic surface, after which they were rinsed with water and dried at 100°.

The gain plates of the copper coulometer were washed

---

[1] Received June 22, 1921.

[2] Published as Contribution No. 39 from the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology.

[3] Wilson and Horsch, *Trans. Am. Electrochem. Soc.*, **35** (1919), 371.

[4] *Chem. Met. Eng.*, **21** (1919), 680.

[5] *J. Phys. Chem.*, **24** (1920), 608.

first with distilled water, then with alcohol, dried by burning the latter, and weighed. The gain in weight gave an accurate measure of the quantity of electricity passed through each cell.

The amount of permanganate produced during the run was obtained by a calculation based on the total weight of the anolyte and the analysis of a weighed sample of the latter. In order to obtain a sample which was representative, the anolyte was stirred thoroughly and allowed to stand for about 30 min. After the small amount of sludge had settled, the sample was pipetted from the clear supernatant solution.

The method of analyzing for permanganate was to wash the weighed sample (about 2 g.) into a 300-cc. flask, dilute to about 100 cc., acidify with glacial acetic acid, add an excess of potassium iodide solution, and titrate with sodium thiosulfate, using starch as an indicator. In base solutions where some manganate undoubtedly was present with the permanganate, the calculation was still made in terms of permanganate.

The total base content was determined in another sample by adding an excess of standard sulfuric acid, and a slight excess of hydrogen peroxide to reduce the permanganate, after which a titration was made with standard sodium hydroxide solution using methyl orange indicator. A blank test of the acidity of the hydrogen peroxide was made, and the amount of acid used up during the reduction of the permanganate by the H_2O_2[1] was, of course, taken into consideration in the calculation.

[1] $2\overset{-}{MnO_4} + 5H_2O_2 + 6\overset{+}{H} = 2\overset{++}{Mn} + 5O_2 + 8H_2O$

RESULTS AND CALCULATIONS

GENERAL DISCUSSION—The main reaction which takes place in the cell as a whole may be represented by the equation:

$$Mn + \overset{-}{OH} + 3H_2O = \overset{-}{MnO_4} + \frac{7}{2} H_2$$

This is accompanied by the passage of 7 faradays of electricity. At the cathode the only reaction is the evolution of hydrogen.

In addition to the oxidation of Mn to $\overset{-}{MnO_4}$, a number of other reactions always take place at the anode. The principal side reactions are the formation of oxides of manganese, iron, and perhaps silicon and carbon, and the evolution of oxygen. (In strongly alkaline solutions some $\overset{-}{MnO_4}$ is also formed.) The mixture of the three metallic oxides is deposited as a sludge. Considerable oxygen was evolved in all the runs made.

The current used up in these side reactions represents the degree of inefficiency of the process. There is little chance of being able to oxidize the manganese of the anode without simultaneously oxidizing its other constituents. Consequently, the losses might be divided into two classes—those theoretically avoidable and those probably unavoidable. The evolution of oxygen and the formation of manganese dioxide belong to the former; the other side reactions mentioned, to the latter. In this paper, however, the calculation of the current efficiency is based on the assumption that the passage of one faraday would produce, in a perfect electrolytic process, one-seventh of a mole of permanganate.

Current efficiency is influenced mainly by variations in four factors, namely, anode composition, electrolyte, temperature, and current density. These are considered below in the order named. Besides the current efficiency, the cell voltage, material efficiency of the anode, and the energy consumption per unit weight of product also are influenced by these four factors. The voltage, and consequently the energy consumption, may be affected somewhat by the material of which the cathode is composed, as a result of the change in hydrogen overvoltage thereby produced. This effect is relatively small, however, and practical considerations limit the choice to iron.

Material efficiency is taken as the per cent of anode manganese which is converted to permanganate. This quantity is not easily determined with precision, owing to the difficulty of reproducing the same anode conditions before and after a run, for the purpose of obtaining the loss in weight. Thus, there is no way, apparently, of removing the coating which always collects on the anode without also removing a small amount of the metal; sometimes solution is absorbed by the anode as a result of its porosity, and this changes its apparent weight on drying; finally, even with physical conditions at their best, there exists the mathematical disadvantage that the difference between initial and final weights was in the neighborhood of 1 g., while the weight of the anode itself was about 800 g., so that errors of weighing were highly magnified.

In spite of these difficulties, however, fairly concordant values were obtained by treating the anode after each run in the manner described above. The results obtained in carbonate solutions showed better concordance than those in base solutions.

EFFECT OF ANODE COMPOSITION—The anodes used in these experiments were made by casting ferromanganese in graphite molds, the castings being cooled slowly over a period of 15 hrs. by burying them in asbestos-magnesia powder while they were still at a red heat. Unless this precaution was taken, the castings cracked spontaneously. Using this method, however, it was found possible to cast alloys containing manganese to the extent of 95 per cent.[1]

The most important variable in the composition of the anode is the ratio of manganese to iron present. The effect of varying the manganese content of the ferromanganese was studied in this laboratory,[2] electrolyses being conducted with anodes containing from 60 to 94 per cent manganese. The anolyte was 12 per cent sodium carbonate solution (previously found to give about the optimum results), and the catholyte was 8 per cent sodium hydroxide solution. The current density was 9 to 10 amp. per sq. dm.; temperature, 25° C.; the results are given in Table I and are shown graphically in Fig 1. It will be noted from the table that the percentages of silicon and of carbon are nearly the same in all the electrodes, the small differences probably being insufficient to produce a noticeable effect on the results. The percentage of iron, therefore, increased as that

TABLE I EFFECT OF VARIATIONS IN ANODE COMPOSITION ON CURRENT EFFICIENCY, VOLTAGE, AND ENERGY CONSUMPTION

Initial anolyte, 12 per cent (1 3 M) Na_2CO_3 solution.
Temperature, 25° C.
Current density, 10 amp./sq dm.

Constituents of Anode Per cent Mn	Si	C	Fe	Current Efficiency Per cent	Cell Voltage	Energy Consumption Kw.Hr.–Kg.
60.2	2.07	5.86	31.8	10.34	5.63	71.9
70.4	1.88	4.93	22.8	28.0	5.84	27.6
75.3	0.64	5.98	18.0	34.0	5.98	23 2
80 4	1.62	3.53	14.4	38.7	5.93	20.3
89.2	1.43	2.65	6.7	45.3	5.57	16.2
94.4	0.68	5.08	0.0	50.1	6.18	16.3

---

[1] The casting process consisted simply in heating the alloy in a graphite crucible in an electric furnace of the resistant type and pouring the melt directly into the open mold. For the 2.5 cm. × 2.5 cm. × 15 cm. electrodes, no scavenger was necessary. In order to cast large bars (4 cm. × 12.5 cm. × 100 cm.) of 80 per cent manganese content, Dr. C. J. Fink (who gave assistance in this phase of the war problem) showed that it was necessary to employ aluminium as a scavenger during the melting and also just before pouring.

[2] Thesis by A. J. Hartsook, M. I. T., 1920.

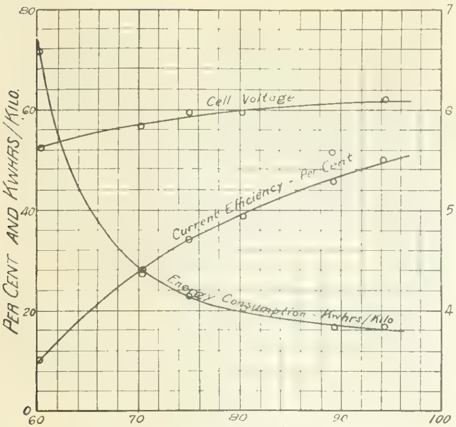


Fig. 1—Showing relation of cell voltage, current efficiency, and energy consumption to manganese content of ferromanganese anode. Temperature, 25° C. Initial anolyte, 12 per cent Na_2CO_3 solution

of manganese diminished. The ratio of manganese to iron in the anode has a marked effect on the current efficiency, the latter increasing with increase in this ratio, as would be predicted. An experiment with spiegel iron (about 40 per cent Mn) showed practically zero yield of permanganate. The effect on cell voltage is small. There is, however, a definite upward trend in the voltage curve with increase in the manganese content. Since the dilution of manganese with iron ought to decrease rather than increase the tendency of the manganese to form permanganate, the slight increase in cell voltage as the manganese content increases appears to be due to a change in overvoltage. The increase in current efficiency, then, apparently is due to the combined effect of two factors, *viz.*, the higher concentration of manganese in the anode and the higher oxygen overvoltage.

The highest concentration of manganese which is readily obtainable commercially is 80 per cent. Higher concentrations are occasionally obtainable, but usually recourse must be had to the expensive "thermit" process. The additional cost for, say, 95 per cent manganese as against 80 per cent would more than offset the gain in production, for, although the current efficiency increases from 40 per cent to 50 per cent, the energy consumption is reduced only from 20 to 18 kw.hr. per kg.

Besides being more costly, the alloys of high manganese content have the mechanical disadvantage of being much more brittle. Hence, commercial ferromanganese was employed in the present investigation (except for the work by Mr. Hartsook just described), the composition being approximately

	Per cent
Mn	75
Fe	16.2
Si	2.3
C (by difference)	6.5

A small amount of work also was done to show the effect of adding other metals to the ferromanganese. The addition of a small percentage of copper had an unnoticeable effect on the current efficiency. Cobalt, when present to the extent of 1 or 2 per cent, reduced the efficiency practically to zero.

EFFECT OF ANOLYTE COMPOSITION—In general, it may be stated that suitable initial anolytes are the solutions of any salts which hydrolyze to give a basic reaction. Thus, in some unpublished work by Dr. B. F. Lovelace at Johns Hopkins University, it was found that with sodium acetate solution a current efficiency of 32 per cent could be obtained. Borax solution gave 35 per cent and disodium phosphate 22 per cent. Using ammonium carbamate solution, the authors were able to obtain fair yields provided the temperature was kept low (around 10° C.). At room temperature, ammonium permanganate decomposes rapidly.

In the practical production of sodium or potassium permanganate, it is desirable to use the solution of a salt, the anion of which will be eliminated automatically, if possible, in the ordinary course of the electrolysis. This may be accomplished by employing the carbonate or hydroxide of the alkali metal, which also has the advantage of being cheaper than any of the other possibilities. The present work is concerned chiefly with experiments with these two species of solution.

TABLE II—RELATION OF CURRENT EFFICIENCY, CELL VOLTAGE, AND ENERGY CONSUMPTION TO THE CONCENTRATION OF CARBONATE IN THE ANOLYTE

Temperature, 25°C., Current density, approx., 7.5 amp./sq. dm.

Average Conc Moles per Liter	Carbonate Per cent	Current Efficiency Per cent	Cell Voltage	Energy Consumption Kw.Hr.Kg.
		$NaMnO_4$		
0.28	2.88	35.5	15.3	57.0
1.10	10.50	32.7	10.0	40.5
1.50	14.1	30.3	8.4	36.6
2.11	18.4	28.5	7.9	36.7
		$KMnO_4$		
0.30	4.07	36.1	12.2	46.5
0.60	7.97	31.3	8.7	33.0
1.55	18.25	28.3	6.3	26.4
2.34	25.9	31.2	5.9	22.4
2.81	29.95	28.5	5.4	22.5
3.26	33.5	29.3	6.1	24.7
3.87	38.3	19.8	6.1	36.5
5.48	49.3	13.2	7.1	63.8

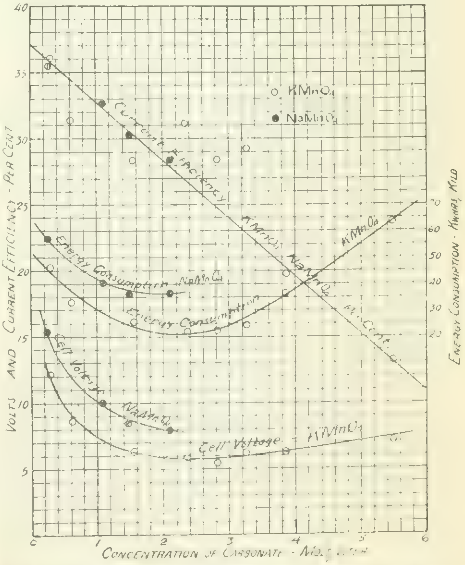


FIG. 2—VARIATION OF CURRENT EFFICIENCY, VOLTAGE, AND ENERGY CONSUMPTION WITH CONCENTRATION IN PURE CARBONATE ANOLYTE. TEMPERATURE, 25° C. C.D., 7.5 AMP. PER SQ. DM.

---

[1] The current density in runs recorded in this and the following section was estimated on the assumption that the front face and one-half the two side faces of the anode were active. In other words, with an anode of square cross section, the active surface was taken as approximately twice the submerged area of the face toward the cathode. This was justified by the appearance of the anode after electrolysis. While this method of calculation may not be very accurate, it does not alter the *relative* magnitude of results.

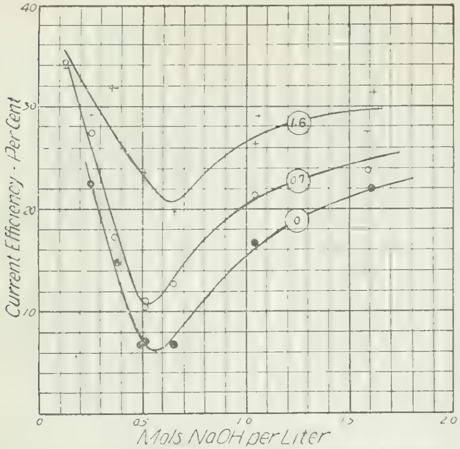


FIG. 3—CURRENT EFFICIENCY IN SODIUM HYDROXIDE ANOLYTES OF VARIOUS CONCENTRATIONS CONTAINING VARIOUS AMOUNTS OF SODIUM CARBONATE. CIRCLED NUMBERS INDICATE MOLAL CONCENTRATION OF CARBONATE. TEMPERATURE, 22° TO 25° C.

The effect of varying the concentration of pure carbonate anolytes is shown by the results given in Table II, which are also presented in graphical form in Fig. 2.[1]

Although the results with potassium carbonate are not as uniform as could be desired, there is no doubt about the general character of the curves. The variations in voltage between the different solutions are due almost entirely to the variations in their conductivity. Thus, potassium carbonate always has a higher conductivity than a solution of sodium carbonate of the same molal concentration, and potassium carbonate solutions have a maximum of conductivity at about 3.1 molal, which agrees fairly well with the location of the minimum of the voltage curve in Fig. 2. It should be noted that for minimum energy consumption at 25°C., one should employ 2.1*M* carbonate solutions. This is practically saturation for sodium carbonate. The energy consumption was calculated in each case from the actual voltage and the corresponding current efficiency as taken from the curve.

It was found that the carbonate electrolyte (as compared with the hydroxide) gives the purest product—uncontaminated with manganate—at the best efficiencies and for the least expenditure of power. Hence, this electrolyte is recommended for technical operation.

The results with hydroxide anolytes, on the other hand, show clearly why such solutions are unsuited to technical operation, and exhibit phenomena which are very interesting from a purely electrochemical viewpoint. With concentrations of sodium hydroxide solutions ranging from about 0.1*M* to 8*M*, it was found that the current efficiency-concentration curve passed through a sharp minimum[2] at about 0.5*M* when the current density was 7.5 amp. per sq. dm. A series of experiments[3] in which the gas evolved at the anode was measured and analysed showed that the low efficiency near the minimum was due to a greater proportion of the current going to oxygen evolution. If carbonate was present in addition to hydroxide, the only effect on this curve was to raise it as a whole without changing its general V-shape. The amount of raising was greater the higher the carbonate concentration. This is brought out by Fig. 3, plotted from the data of Table III. These V-shaped curves were obtained with potassium as well as sodium hydroxide, the curves for the respective hydroxides being nearly, but not exactly, coincident. It seemed probable, therefore, that the effect was due to conditions brought about by the hydroxyl-ion concentration; and the results have been plotted accordingly with $\bar{OH}$ concentrations as abscissae. The $\bar{OH}$ concentration was calculated from the degree of dissociation based on conductivity data. Fig. 4 shows the

TABLE III—CURRENT EFFICIENCY IN SODIUM HYDROXIDE ANOLYTES OF VARIOUS CONCENTRATIONS[1] AND CONTAINING VARIOUS AMOUNTS OF SODIUM CARBONATE. TEMPERATURE 22° TO 26°C.

Initial Anolyte Moles Na_2CO_3 per Liter	Initial Anolyte Moles NaOH per Liter	Current Efficiency Per cent	Initial Anolyte Moles Na_2CO_3 per Liter	Initial Anolyte Moles NaOH per Liter	Current Efficiency Per cent
0.0	0.25	22.6	1.3	0.13	32.6
	0.51	7.1		0.31	26.8
	1.04	16.6		0.52	15.6
	1.60	22.0		1.04	23.5
	2.18	26.1		1.59	26.3
	0.38	14.7		2.10	27.8
	0.49	6.9		0.33	28.7
	0.65	6.9		0.53	27.4
				0.66	16.6
0.7	0.13	34.2		1.05	25.0
	0.25	27.5		1.59	29.2
	0.51	10.7		2.19	29.1
	1.04	21.6		0.27	34.8
	1.59	23.8		0.47	24.0
	2.25	27.3		0.53	15.6
	0.36	17.2		1.04	27.2
	0.51	10.9		1.60	29.3
	0.65	12.8			
			1.6	0.13	33.8
1.0	0.15	33.2		0.25	29.3
	0.28	31.7		0.51	23.1
	0.51	23.6		1.04	26.4
	1.00	24.4		1.59	27.7
	1.60	26.9		2.14	26.9
	2.00	28.3		0.36	31.8
	0.13	35.1		0.51	23.7
	0.25	32.4		0.65	19.9
	0.51	19.8		1.06	29.2
	1.04	24.6		1.62	31.5
	1.58	26.7		2.19	32.8
	2.09	28.3			

[1] In these experiments the sodium hydroxide content was not maintained constant during a run as it was in the experiments of Tables IV and V.

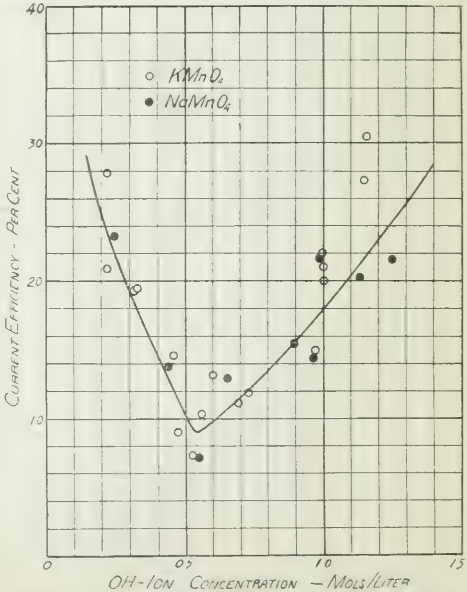


FIG. 4—CURRENT EFFICIENCY VS. OH-ION CONCENTRATION FOR BOTH $NaMnO_4$ AND $KMnO_4$ PRODUCTION IN PURE HYDROXIDE ELECTROLYTES. TEMPERATURE, 25° C. C.D., 7.5 AMP. PER SQ. DM.

---

[1] See second column, page 765.

[2] In similar electrolyses where anodes of ferrochronium were oxidised to chromic acid in alkaline solution, a similar minimum was found at certain concentrations of hydroxide. (Unpublished thesis by R. R. Ridgway, M. I. T., 1920.)

[3] Thesis by M. M. Whitaker, M. I. T., 1920.

results for pure sodium and potassium hydroxides. The two sets of data for this curve are given in Table IV. In each run, the hydroxide concentration was kept sensibly constant by adding the proper amount of concentrated caustic solution at small, regular time intervals (about 20 min.). The impossibility of accomplishing this accurately is probably responsible for the unusually large deviations observed in these experiments.

Certain theories as to the fundamental cause of the minimum point and peculiar shape of these curves are being tested out, and will probably form the basis of a later article.

TABLE IV—RESULTS OF EXPERIMENTS WITH PURE HYDROXIDE SOLUTIONS AS ANOLYTES

Temperature—25° C.; cell current—5 amp.; current density—7.5 amp. sq. dm.

Final Conc. $KMnO_4$ $(NaMnO_4)$ Per cent	Av. Conc. KOH (NaOH) Per cent	Av. Conc. KOH (NaOH) mole liter	Degree of Dissociation	Av. Conc. OH Moles Liter	Current Efficiency Per cent	Cell Voltage	Energy Consumption Kw.Hr./Kg	Material Efficiency Per cent
				$KMnO_4$				
0.345	1.43	0.26	0.858	0.22	21.2	10.0	55.8	61.0
0.447	1.45	0.26	0.858	0.22	27.9	9.7	41.2	65.6
0.317	2.16	0.39	0.830	0.32	19.4	7.9	48.3	56.6
0.317	2.25	0.40	0.830	0.33	19.6	8.4	50.8	56.7
0.234	3.12	0.57	0.804	0.46	14.5	6.2	50.8	53.5
0.141	3.21	0.59	0.802	0.47	9.0	6.7	88.3	48.6
0.123	3.53	0.65	0.797	0.52	7.4	6.2	99.3	100 +[1]
0.170	3.88	0.71	0.790	0.56	10.3	5.9	67.9	51.3
0.202	4.24	0.77	0.780	0.60	13.4	5.4	47.8	79.4
0.177	4.77	0.90	0.765	0.69	11.2	5.3	56.2	52.6
0.179	5.20	0.96	0.760	0.73	11.9	5.1	50.8	86.2
0.255	6.97	1.35	0.718	0.97	15.0	5.1	40.4	48.7
0.304	7.19	1.38	0.716	0.99	22.0	5.3	28.6	
0.269	7.25	1.40	0.715	1.00	20.0	5.6	33.2	
0.281	7.36	1.41	0.715	1.01	20.5	5.3	30.7	
0.435	8.48	1.64	0.695	1.14	27.3	4.4	19.1	72.0
0.510	8.67	1.68	0.688	1.16	30.5	4.3	16.7	83.6
0.384	12.25	2.48	0.622	1.61	27.0	4.1	18.0	91.5
				$NaMnO_4$				
0.352	1.17	0.295	0.802	0.237	23.2	10.5	59.8	68.5
0.205	2.24	0.572	0.763	0.437	13.8	7.3	70.0	78.4
0.120	2.82	0.73	0.742	0.541	7.16	6.9	127.5	70.0
0.187	3.52	0.915	0.713	0.653	13.0	5.8	59.1	61.4
0.219	5.08	1.34	0.670	0.898	15.6	5.3	44.9	69.3
0.221	5.46	1.45	0.660	0.960	14.7	5.0	45.0	65.2
0.269	5.64	1.50	0.655	0.984	21.9	5.3	32.1	
0.304	6.83	1.85	0.610	1.13	20.3	5.0	32.6	74.0
0.279	7.83	2.13	0.585	1.25	21.5	4.7	29.0	76.0

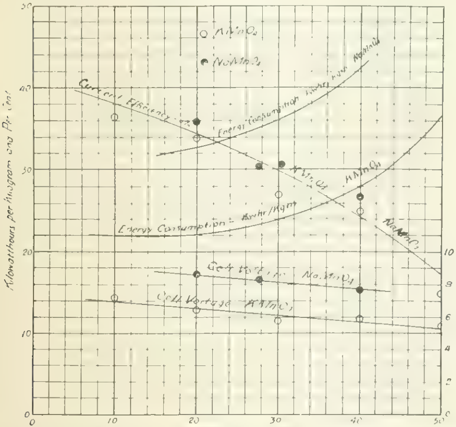


FIG. 5—VARIATION OF CURRENT EFFICIENCY, VOLTAGE AND ENERGY CONSUMPTION WITH TEMPERATURE. ANOLYTES: K_2CO_3, 14 PER CENT, NA_2CO_3, 12 PER CENT; C. D., 6 TO 9 AMP. PER SQ. DM.

EFFECT OF TEMPERATURE—The effect of variation in temperature upon current efficiency, voltage, and energy consumption is shown graphically in the plot in Fig. 5 (data in Table V). These experiments were made with carbonate solution (K_2CO_3 and Na_2CO_3) for anolyte, since carbonate was found to be the best anolyte for commercial use, and gave no peculiar variations as did hydroxide solutions. All the runs were of 5 hrs. duration, with an anodic current density of 6 to 9 amp. per sq. dm. Each result in the table represents the average for *six* cells in series, except at 40° where three cells were operated for $NaMnO_4$ and three for $KMnO_4$. The anolyte concentrations were 14 and 12 per cent potassium and sodium carbonate, respectively. The variation in current density was due to differences in size of electrodes. As will be seen later, variation of current density between these limits has little effect on current efficiency.

TABLE V—RESULTS OF EXPERIMENTS AT VARIOUS TEMPERATURES

Cell current—5 amp.; current density—6 to 9 amp. sq. dm.

Anolyte	Temp. °C.	Current Efficiency Per cent	Cell Voltage	Energy Consumption Kw.Hr./Kg.	Material Efficiency Per cent
14% K_2CO_3	10	36.4	7.2	21.3	86.8
	20	33.9	6.5	22.1	...
	30	27.0	5.8	24.2	.
	40	24.8	5.9	27.9	70.6
	50	14.9	5.4	36.3	..
12% Na_2CO_3	20	35.9	8.6	32.7	.
	27.5	30.5	8.3	35.4	57.0
	30.5	30.7	9.8[1]	36.3	68.2
	40	26.7	7.5	42.4	67.6

[1] Exceptionally high for some unknown reason and hence not plotted.

It will be noted that both current efficiency and cell voltage are reduced as the temperature increases. The cell voltage is lower chiefly because of the lessened resistance of the solution, but the oxygen overvoltage is also less at high temperature. This latter lowering and the more rapid decomposition of permanganate at high temperatures are responsible for the decrease in efficiency as the temperature increases, the former being the more important.

Although these results seem to indicate that the efficiency of sodium permanganate production is slightly greater than for potassium, the difference is probably not greater than the experimental error; furthermore it did not show up in other series. Only one curve is drawn to represent the average results.

In plotting the data, the best current efficiency-temperature and voltage-temperature curves were drawn through the points obtained, and values read from these curves were used in calculating the values for energy consumption which consequently lie upon a smooth curve.

The results indicate that the maximum current efficiencies and minimum energy consumptions are obtained at temperatures below 10°C., although the energy consumption varies but little up to 20°C.

EFFECT OF CURRENT DENSITY—By passing various currents through a cell of given dimensions the effect of varying the current density has been determined. In this way both the anodic and cathodic current densities were altered simultaneously, but since it is inconceivable that the cathodic current density can have any effect on the current efficiency, the results are interpreted to represent the effect of variations in anodic current density.

In the case of these experiments a different set of anodes and a different size and type of cell were used. This was done partly in order to obtain more accurate figures for current density, and partly in order to see whether the results obtained up to this time could be duplicated with much larger cells. The cell was constructed of concrete lined with paraffin. A diaphragm composed of a sheet of asbestos paper between two supporting sheets of asbestos cloth divided the cell into two compartments. The anode was made up of two bars each about 12 cm. in width, submerged to a depth of about 25 cm. This was placed close to the diaphragm so that only the front surface was very active. The value of the anodic current density is taken as the apparent current density obtained by dividing the cell current by the actual area of the submerged portion of the anode on the side toward the diaphragm.

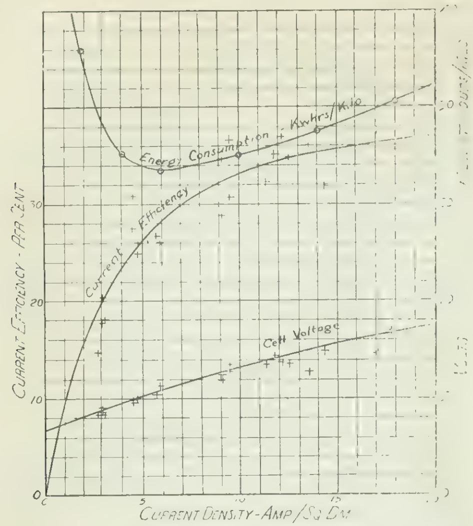


FIG. 6—SHOWING THE EFFECT OF VARIATIONS IN CURRENT DENSITY ON CURRENT EFFICIENCY, CELL VOLTAGE, AND ENERGY CONSUMPTION. INITIAL ANOLYTE, 15 PER CENT Na_2CO_3 SOLUTION. TEMPERATURE Temperature 30° C.; initial anolyte 15 per cent Na_2CO_3 solution

The runs were all made at a temperature in the neighborhood of 30° and the results corrected to this temperature on the basis of the data given in Table VI. The initial anolyte in each run was approximately 15 per cent Na_2CO_3 solution. No experiments were made with the potassium salt. The final permanganate content of the runs reported here never exceeded about 3 per cent $NaMnO_4$.

The data given in Table VI are plotted in Fig. 6. The plot shows the energy consumption curve to possess a minimum of 23.5 kw. hr. per kg. when the current density is 6 amp. per sq. dm. The energy consumption increases gradually with increase in current density beyond this point. Since the current efficiency also continues to increase, the optimum current density for technical operation will be somewhat above 6 amp. per sq. dm. because of the saving in cost of installation thereby effected.

TABLE VI EFFECT OF VARIATIONS IN CURRENT DENSITY

Temperature 30° C.; initial Anolyte 15 per cent Na_2CO_3 solution

Current Density Amp Sq Dm	Current Efficiency Per cent	Cell Voltag	Energy Consumption Kw Hr Kg.
2 69	14.8	4 22	37 6
2.9	20 3	4.30	28 0
2.9	17.8	4.60	34.2
3.0	18.0	4.25	31.2
4.51	27.6	4.95	23 7
4 51	30 9	4.90	21.0
4.73	26 0	5.00	25 5
4.73	24.8	5.00	26.7
5.70	26.6	5 30	26.4
5.91	26 1	5.70	28 9
9.03	34.7	6.25	23.8
9.03	28 9	5.90	27 0
9.46	36.7	6.30	22.7
9.46	30.4	6 75	29 4
11.3	32 3	6.70	27 5
11.8	35.2	7.20	27.1
12 1	37.0	6.90	24 7
12.5	34.8	6.80	25 9
13 5	36 0	6.40	23 5
14.3	31.9	7.45	30 9
17 0	37 5	7 30	25 8
17.8	35.6	8 50	31 6

Extrapolation of the voltage-current density curve indicates that the cell voltage when C. D. = 0 is 3.4 volts as compared with a theoretical value[1] of 1.07 volts. The overvoltages probably are large, but several other effects undoubtedly enter to help make up the 2.3 volts difference between these two values.

Two other series of runs were made in which the average permanganate concentrations were about 4 and 8 per cent, respectively. On account of inaccuracies introduced in the analytical determinations, the results were not even as concordant as those where the permanganate concentration was low. Within the experimental error there was substantially the same current efficiency at all concentrations of permanganate. This conclusion is substantiated by the results obtained in the long-time runs discussed below.

THE "SKIN EFFECT" AND ITS ELIMINATION —The requirement of simplicity in commercial operation demands that the anodes may be kept in action continuously until they have been reduced to a small fraction of their initial size. In the earlier stages of this investigation, a good deal of trouble was encountered, in runs of more than a few hours' duration, by a "skin effect" which was exhibited by the ferromanganese anode. The anodes always became covered with a coating of oxide which, when thin, adhered too firmly to be scraped off. The coating developed more rapidly, and to a greater extent, in caustic than in carbonate anolytes. In carbonate anolytes, electrolysis would proceed smoothly, in spite of the coating, for 25 or 30 hrs., after which the voltage would commence to rise rapidly and severe heating ensue so that the cell had to be shut down. In the semi-plant scale experiments which were conducted in connection with the war work, a sharp rise in the voltage-time curve of a given cell was the signal for the removal of its anode and the substitution of a fresh one, the particular cell being meantime by-passed so that the current in the series was not interrupted. The "fresh" anode was prepared by removing the coating with a sandblast, which made it ready for another 30-hr. operating period. It should be understood that this active operating period was not absolutely regular, but 30 hrs. represents a fair average. As the permanganate concentration increased, the period became somewhat shorter.

Other methods than sandblasting were tried for removing the coating. Thus, the coating formed in carbonate electrolytes became very flaky on drying and was nearly all easily removed by scraping with a cold chisel. The surface of the anode was then ground slightly all over with a carborundum wheel. Another method was to "pickle" the anode in hydrochloric acid. Sandblasting was the least undesirable of all these methods from the technical viewpoint.

It was attempted to obviate the formation of the oxide coating by the use of "addition agents" in the electrolyte. No improvement was brought about, however, by the use in this way of such salts as chlorides, chlorates, perchlorates, sulfates, and nitrates. Incidentally, it was found that perchlorates and nitrates to the extent of about 1*M* in 2*M* hydroxide solutions reduced the efficiency to zero, while with sulfate and chlorate in similar concentration, the current efficiency was only about 2 per cent less than with carbonate.

---

[1] For the calculation of the theoretical value the cell was considered to be constituted as follows:

$\overline{Mn_2}$ MnO_4 (0.1*M*), CO_3 (0.5*M*) OH (1*M*), H_2 (1 atm.) Pt.

The liquid junction potential, which would be of the order of magnitude of two or three hundredths of a volt, was neglected. It was assumed that the potential of manganese vs. MnO_4 in a half-molal carbonate solution would be the same as in a base solution where the O-H concentration is 10^{-6}*M*. The potentials involving manganese were calculated from data in *Abhand deutsch. Bunsen-Ges.*, II, 5 (1911), 201. The potential ½ H_2 + [illegible] = H (1-*M*), was taken as zero. The e. m. f.'s of the two "half" reactions are:

Mn + 7 [illegible] + 8 O-H (10^{-6}*M*) = MnO_4 (0.1*M*) + $4H_2O$; E_1 = 0.243 volt

$\overline{H_2O}$ = O-H (1*M*) + [illegible] 8 OH + ½ H_2; E_2 = 0.826 volt.

$\overline{Fro}$ the whole cell, therefore, E = E_1 + E_2 = 1.069 volts.

The clue which led to the discovery of the conditions for eliminating the coating was furnished by a 5-hr. electrolysis with a potassium carbonate solution of higher concentration than had been used previously (namely, 30 per cent K_2CO_3), at the end of which it was found that the anode surface, after the adhering permanganate solution had been rinsed off, was brightly metallic and free from the usual coating. Further experiments showed that under the following conditions of temperature and *initial* anolyte, electrolysis proceeds smoothly and continuously for an indefinite length of time without coating formation:

Product	Anolyte	Temperature
$KMnO_4$	30% K_2CO_3 solution	28° C. or lower
	15% K_2CO_3 solution	12° C. or lower
$NaMnO_4$	Saturated (7%) Na_2CO_3 solution	10° C. or lower

Short periods of operation at 10° higher than the above temperatures were harmless in the case of potassium.

If it is desired to build up a concentration of *sodium* permanganate above about 3 per cent, however, it is necessary to add solid Na_2CO_3 to the anolyte from time to time. While not many of these long, continuous runs (7 to 10 days in duration) were made, nevertheless sufficient data were obtained to indicate that the current efficiency and energy consumption under such conditions are about the same as in the runs on which the curves presented in this paper are based, and the anodes are clean and bright at the end of the operation.

SUMMARY

1—The foregoing article presents in tabular and graphic form the results of extensive experimental work on the more important factors involved in the electrolytic production of sodium and potassium permanganates from ferromanganese anodes.

2—In the investigation of the effect of *anode composition* it was found that the higher the manganese content of the electrode, the higher the current efficiency, anodes containing less than 40 per cent giving practically no yield under any conditions. Other constituents at the anode seem to have comparatively little effect except in the case of cobalt, about 2 per cent of which practically destroys the permanganate producing power of a ferromanganese electrode. In view, however, of the greater cost and brittleness of anodes containing more than 80 per cent manganese, the commercial 80 per cent ferromanganese appears to be the best anode material for technical operation, and most of the experiments were made with such anodes.

3—Possible *anolytes* are alkali metal salts of weak acids, and alkali metal hydroxides. The best anolyte appears to be a solution of alkali metal carbonate, the carbonate being destroyed in the course of electrolysis and replaced by permanganate uncontaminated by manganate or other salts. Hydroxide solutions are interesting from the theoretical viewpoint, in that they give a sharp minimum in current efficiency at an intermediate OH concentration.

4—The operating *temperature* should be as low as possible (10° to 20°C.). Low temperature gives highest efficiency and lowest energy consumption, and makes possible the continuous operation of the anode (provided the initial carbonate concentration is high). High temperature gives lower current efficiency and promotes a "skin effect" on the anode surface which gives rise to excessive voltages.

5—A *current density* of about 6 amp. per sq. dm. gives the minimum energy consumption. The optimum operating current density is somewhat higher than this. At lower current densities the current efficiency falls off rapidly; at higher current densities it rises slowly, but the increased I. R. drop through the solution results in somewhat higher energy consumption.

6—It is believed that the effect of practically all variables (such as temperature, current density, anolyte composition, etc.) on the current efficiency is in reality due to the variations which these factors cause in the oxygen overvoltage, a high oxygen overvoltage being necessary for high current efficiencies in permanganate production. It is hoped to present further evidence bearing upon this point in a later paper.

7—The essential conclusions as to the optimum operating conditions and the efficiencies obtainable have all been confirmed by continuous operation of a full-sized commercial cell, using five ferromanganese bars, each 5 in. × 1.5 in. × 35 in., as the anode.

Bakelite Company Wins Decree

The General Bakelite Company of New York was awarded a decree in its suit against the General Insulate Company of Brooklyn charging infringement of three Bakelite patents. The decision against the defendant was handed down by Judge I. Chatfield of the United States District Court, Eastern District of New York, on August 2, 1921.

The three Bakelite patents involved were No. 942,699, 492,852 and 939,966 commonly designated as the Heat and Pressure Patent, the Fibrous Materials or Indurated Product Patent and the Comminuted Mixture or Molding Patent, all of which have been sustained and declared infringed by the Court.

The decision is remarkable for the comprehensiveness and the clearness with which Judge Chatfield has handled a highly technical subject, involving fine distinctions between chemical and physical processes and between actual inention and the manufacture of a known substance by variations in technique of production. Particular interest is attached to this decision because the defendant in the case—General Insulate Company—is a molding concern doing business in Brooklyn, New York, and using the products manufactured by the Redmanol Chemical Products Company of Chicago and as Judge Chatfield said in his opinion:

"The record shows that in fact the Redmanol Company has stood behind the defendant in the trial of this action, and in so far as investigation of the prior art and discussions of questions of patentability are concerned, the Redmanol Company has as freely and fully presented its evidence as if the action had been against the Redmanol Company for infringement of the plaintiff's patents in the manufacture of the synthetic gum itself."

The Redmanol Company had no office in New York—hence the indirect action of the General Bakelite Company in filling a Bill of Complaint against one of the users of the Redmanol products. The Bill of Complaint was filed September 18, 1917, but a trial could not be obtained until March 31, 1919. The trial lasted many weeks in open court, the final arguments taking place on June 22, 1919.

The decision itself covers 36 printed pages, and reviews the various patents that have been issued both in the United States and foreign countries for the preparation of materials generally classified as synthetic resins. The fact that the Baekeland patents go further than any previous patents in covering the preparation of materials that are of practical value and prepared according to exact processes yielding definite products, is definitely shown. The decision is a valuable contribution to chemical patent literature.

The Detection of Carbon Monoxide[1,2]

By C. R. Hoover
Department of Chemistry, Wesleyan University, Middletown, Connecticut

The problem of detecting quantities of carbon monoxide too small to be determined accurately by the ordinary methods of gas analysis, yet sufficiently large to produce harmful physiological effects, has been attacked by a number of investigators.

Several forms of portable apparatus for the detection of carbon monoxide in houses, mines, factories, etc., have been devised.

Racine[3] attached a filament of guncotton dusted with platinum black to the terminals of an electric circuit in such way that as the guncotton was ignited by the heat of absorption of the carbon monoxide on the platinum black, the circuit was closed and a signal given. This device is capable only of detecting quantities of carbon monoxide greater than 0.75 per cent and is therefore not sufficiently sensitive for the hygienic testing of air.

Guasco[4] constructed a toximeter for carbon monoxide consisting of two glass bulbs, one coated with platinum black, connected by a U-tube containing a colored liquid. Temperature changes produced by the absorption of carbon monoxide on platinum bulb altered the level of the liquid in the U-tube. Although Guasco claims to be able to recognize 0.01 per cent of carbon monoxide with this apparatus, it is difficult to manipulate, and useless in most industrial gas mixtures.

Lamb and Larson[5] have recently investigated the thermometric principle and propose two accurate methods very well adapted t othe continuous analysis of a gas mixture containing carbon monoxide. Their apparatus is not intended to be readily portable, but it would seem to be of special value for stationary use in laboratories and industrial plants for the analysis of combustible gases which can be freed from catalytic poison.

Nowicki[6] patented a pocket apparatus in which strips of paper moistened with palladium chloride solution are placed in a glass tube through which the suspected gas is drawn. However, the slowness of the reaction, the need of freshly preparing the paper to be used out of contact with reducing substances, and the wide variety of reducing substances that produce similar changes to those produced by carbon monoxide, have prevented any considerable practical use of this type of detector.

Harger[7] designed a portable apparatus for the detection of carbon monoxide in mines. The variation in the conductivity of a solution of hydrogen iodide formed from the iodine liberated by the action of carbon monoxide on heated iodine pentoxide is employed to indicate the quantity of the gas present. This method is obviously difficult of manipulation, and the apparatus is expensive and cumbersome.

Teague[8] of the Bureau of Mines has adapted the iodine pentoxide method of analysis to the determination of carbon monoxide in automobile exhause gases by using liquid air to remove interfering substances. A form of portable apparatus has been described, but the manipulation is rather more diffciult than can be carried out by the average working man.

In practical use none of the chemical or thermometric detectors mentioned have been found to be as generally successful as smal animals, especially canaries, as suggested by Burrell, Seibert and Robertson of the Bureau of Mines.[9] That small animals, are, however, unsatisfactory in some cases was first pointed out by the same investigators. A man moving or at work may be overcome before a small animal quietly confined, and a person may be seriously affected by long breathing of low concentration of gas which causes no appreciable symptoms of distress in small animals. Among the other objections, the following may be mentioned: The detection by small animals is applicable only to a limited range of concentration of carbon monoxide, and there is an appreciable difference in sensitiveness of different animals of the same kind. The uncertainty and slowness of recovery of small animals unless placed in pure air or oxygen makes it impossible to make tests at frequent intervals in impure air, or after passing through impure air, without a large number of birds and special containers. When not in use, animals must be cared for at places that are readily accessible. It can therefore be concluded that there is need in many industrial operations of a more reliable, more rapid, and simpler method of detecting carbon monoxide than any yet proposed.

HOOLAMITE

Lamb, Bray and Frazer[1] have summarized the work done by the Defense Chemical Research Section of the Chemical Warfare Service upon the absorption of carbon monoxide. One of the absorbents developed, Hoolamite,[2] was the result of an investigation of the action of carbon monoxide on mixtures of iodine pentoxide and other substances begun in this laboratory during the summer of 1917. This work was continued after September 1917 with the personal coöperation of Lieut. Col. A. B. Lamb, director of Defense Research, as a part of the general investigation described in the article just mentioned. Subsequent to the signing of the armistice and the resulting curtailment of the activities of the Chemical Warfare Service, the problem was continued in this laboratory and the detectors described in this article developed.

COMPOSITION—Hoolamite is prepared by mixing fuming sulfuric acid with iodine pentoxide and an inert supporting material. During the early stages of the development of this absorbent it was noticed that carbon monoxide imparted to the white Hoolamite of certain range of composition colors varying from pale bluish green to brownish black, the depth of the color depending upon the amount of the gas present. The nature of the compounds of iodine and oxides of iodine with sulfur trioxide and sulfuric acid is being investigated, but has not yet been definitely determined. The green color is due to an unstable substance which can be formed from iodine and sulfur trioxide. On standing or gentle warming in the presence of sulfur trioxide, the green material changes to orange yellow and finally, upon the addition of iodine pentoxide, to a white substance. Since at ordinary temperatures Hoolamite oxidizes carbon monoxide to carbon dioxide with the liberation of iodine, if an excess of sulfur trioxide is present, the green substance will be formed and is thus indicative of the presence of carbon monoxide.

Iodine pentoxide and fuming sulfuric acid of high sulfur trioxide content form solid bodies if the weight of acid does not exceed 70 per cent of the weight of the mixture, but in order to produce the green body a greater proportion must be present and such mixtures, being pasty, must necessarily be supported on an inert porous material in order to expose them efficiently to the action of carbon monoxide. Asbestos fiber gives the most active material, but it is difficult to handle, and irregular in surface and, consequently, in action. However, a material almost as active can be prepared with granular pumice stone, and this supporting material is used for all mixtures.

Table I shows the composition of the mixtures found to be best suited to the detection of small amounts of carbon monoxide.

---

[1] Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published by permission of the Director of the Chemical Warfare Service.

[3] *Bull. soc. chim.* (3), **1** (1889), 555.

[4] *Compt. rend.*, **155** (1912), 282.

[5] *J. Am. Chem. Soc.*, **41** (1919), 1908.

[6] *Chem.-Ztg.*, **35** (1911), 1120.

[7] *Iron Coal Trades Rev.*, **88** (1914), 912.

[8] This Journal, **12** (1920), 964.

[9] Bureau of Mines, *Technical Paper*, **62** (1914).

[1] This Journal, 12 (1920), 213.

[2] Lamb and Hoover, U. S. Patents 1,321,061 and 1,321,062.

TABLE I—COMPOSITION OF DETECTOR MATERIAL

Use	Method of Preparation	Iodine Pentoxide Per cent	Pumice Stone Per cent	Fuming Sulfuric Acid Per cent
Approximately quantitative detection of reducing gases—Detector B	Mixed in open vessels	12.0	35.0	53.0(60% SO_3)
Quantitative detection of carbon monoxide—Detector C	Mixed in closed vessels or in air of low humidity	10.6	33.3	56.1(60% SO_3)
Quantitative detection of carbon monoxide—Detector C	Mixed in open vessels High humidity	11.0	34.0	55.0(80% SO_3)

Since Hoolamite is a corrosive, deliquescent material, it must be preserved in closed vessels which are not attacked by acids or oxidizing agents. When so preserved, it gradually increases in activity for several days, finally remaining unchanged apparently indefinitely. The material is usually employed in small glass tubes which are sealed after filling and opened just before use.

SENSITIVITY—Under favorable conditions concentrations of carbon monoxide as low as 0.005 per cent can be detected by the passage of 500 cc. of a gas mixture through a glass tube containing a 50 mm. × 5 mm. column of Hoolamite. The color developed is proportional to the amount of carbon monoxide present and the cross-sectional area of the detector material, for concentrations of carbon monoxide of 3 per cent or less. The rate at which the gas is passed can vary considerably, but for quantitative results it should be kept between 30 and 60 sec. for a 500-cc. sample through a tube of 5-mm. inside diameter. The depth of the detector material should be at least 2.5 cm., 5 to 7 cm. being commonly used. Carbon monoxide reacts readily with the detector material at —10° C. Since the action is strongly exothermic the color produced is largely independent of the temperature. As a result of chemical changes such as were mentioned above, the green color indicating the presence of carbon monoxide disappears in a few minutes and the material can again be used as before. After twelve positive tests, with concentrations of carbon monoxide not greater than 0.2 per cent, the color produced becomes somewhat irregular in shade and a new sample should be employed. With higher concentration of carbon monoxide proportionately less tests can be made with one tube. Twenty to thirty negative tests in ordinary air can be made before the activity of the Hoolamite has been destroyed.

COLOR STANDARDS—Permanent color standards consisting of granules of pumice stone, normal or basic copper acetate, and chromium oxide can be prepared which match closely the colors produced in Hoolamite by a 500-cc. sample of gas containing amounts of carbon monoxide from 0.03 to 0.17, or 0.2 per cent. Above 0.2 per cent for a 500-cc. sample the colors are more irregular, and other methods than direct color comparison give better results.

ACTION WITH OTHER GASES—A substance capable of rapidly oxidizing carbon monoxide at low temperatures can also be expected to react with oxidizable gases and vapors other than carbon monoxide. Unsaturated hydrocarbons, gasoline vapor, hydrogen sulfide, arsine, hydrogen cyanide, and various complex organic compounds, especially those containing halogens or amino nitrogen, are similar in action to carbon monoxide. In the absence of carbon monoxide the material is a sensitive detector for such substances. Fortunately all interfering substances investigated are absorbed by dry active charcoal. Hydrogen, methane, sulfur dioxide, nitric acid, ammonia, and other common gases and vapors are without action.

For the determination of small amounts of carbon monoxide in the laboratory, any simple container from which definite volumes of gas can be forced under a pressure of several inches of water, appropriate color standards, and a few tubes of Hoolamite are all that are necessary. If other reducing gases are present, it is necessary only to pass the mixture to be examined over a column of active charcoal before it comes into contact with the Hoolamite. It may be noted here that a method of determining large amounts of carbon monoxide in the usual type of absorption pipet by means of Hoolamite is also being developed.

POCKET DETECTOR FOR INDUSTRIAL USE

The most important application of Hoolamite that has yet been made is to the industrial detection of carbon monoxide. A simple and durable form of pocket detector, Type B, is shown in Fig. 1. This device is 24 cm. long over all and weighs 260 g. Its construction and operation are explained by Fig. 2. A 250-cc. sample of the gas to be examined is drawn through the guard tube, A, containing active charcoal, by means of ten compressions of the rubber bulb, B, and forced out through the detector material in the glass tube, D. The green color produced in the detector tube is compared with color standards contained in an adjoining tube as shown in Fig. 1. The range of approximately quantitative detection with this instrument is from 0.05 to 1 per cent.

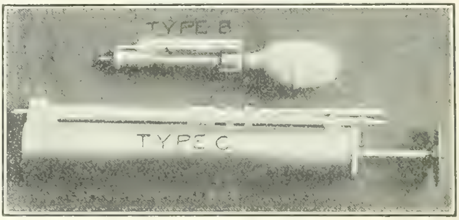


FIG. 1

In practical use this instrument (Type B) has been successful as a qualitative and approximately quantitative detector for carbon monoxide. It is sufficiently sensitive to detect in a few seconds quantities of the gas less than are harmful to men, or capable of causing symptoms of distress in small animals. The directions for use are simple and the instrument can be used by the average workman. With improved Hoolamite and revised directions to insure more definite volumes of gas and rates of passage, it should be increasingly valuable.

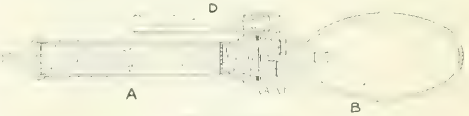


FIG. 2—TYPE B

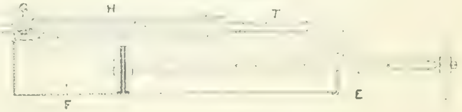


FIG. 3—TYPE C

IMPROVED APPARATUS

It is evident that if the volume of gas and its rate of passage can be regulated more accurately than is possible with the device just described, analytical results of correspondingly greater accuracy will be secured. With this object in view a metal cylinder and piston were substituted for the aspirator bulb and a positively operated stopcock for the rubber valves. The exterior appearance of the improved apparatus is shown in Fig. 1 (Type C). The construction and operation can be understood by referring to Fig. 3. Outward movement of the piston rod, E, draws 500 cc. of gas to be examined through the valve, G, into the cylinder, F. As the piston reaches the end of its travel a rod connected by track and gear to the valve, G, turns it 90°, thus connecting the cylinder with the guard tube, H, and the detector tube, T, through which the gas is passed by the return stroke of the piston. Completion of the stroke moves the valve to its original position.

Among the advantages of this type of instrument may be noted: Definite volume of sample, regular rate of passage governed by the size of the opening into the guard tube, the sample can be taken quickly in a dangerous atmosphere or in the dark, and the analysis made at leisure in a safe, better lighted spot.

As previously stated, concentrations of carbon monoxide greater than 0.2 per cent give somewhat irregular colors when a 500-cc. sample is forced through a 5-mm. tube of Hoolamite; hence with the type C detector the color comparison scale covers only the range from 0.03 to 0.17 per cent. Quantities of carbon monoxide greater than 0.17 per cent are determined by taking advantage of the fact that the color change produced in Hoolamite by a given quantity of carbon monoxide is independent, within the limits previously stated, of the volume of the gas sample, provided the rate of passage is properly regulated. When a sample containing more than 0.17 per cent is being expelled from the cylinder, the color corresponding to 0.17 per cent will be reached before the stroke is completed. Hence by graduating the piston rod of the apparatus (E, Fig. 3) in per cent carbon monoxide, quantities up to 3 per cent can be determined with a good degree of accuracy.

The improved detector has not yet been put upon the market, but practical tests indicate that it is superior in accuracy and range to the smaller, type B, instrument, although somewhat more cumbersome. Table II gives the results of comparative tests of the two detectors which support the statements just made.

TABLE II—COMPARATIVE TESTS OF DETECTORS

Source of Carbon Monoxide	Detector B	Detector C	Iodine Pentoxide Laboratory Analysis
	Per cent	Per cent	Per cent
Pure gas	0.5	0.6	0.583
Flue gas	0.5	0.4	0.431
Illuminating gas	0.3	0.2	0.181
Pure gas	0.2	0.12	0.127
Illuminating gas	0.1	0.07	0.069
Illuminating gas[1]	0.0	0.04	0.034

[1] Charging floor, water gas plant.

The two devices are designed to supplement each other, the simpler being suited to occasional use in the hands of persons engaged in work exposing them to the danger of breathing carbon monoxide such as is met in mines; producer, water, and blast furnace gas plants; garages; boiler rooms; tunnels and excavations near gas mains; army and navy work, etc. The more accurate device is intended to meet the needs of chemists, engineers, inspectors, and other persons responsible for the welfare of workmen, the regulation of plant operations, laboratory tests, and the conduct of industrial research.

SUMMARY

1—A mixture of pumice stone, iodine pentoxide, and fuming sulfuric acid reacts with carbon monoxide to give a green color varying in depth with the concentration of the gas.

2—Two portable devices by means of which this reaction can be applied to the approximately quantitative determination of carbon monoxide are described.

The Determination of Tannin[1, 2]

By John Arthur Wilson and Erwin J. Kern

LABORATORIES OF A. F. GALLUN & SONS CO., MILWAUKEE, WISCONSIN

A rather widespread controversy has arisen over a new method of tannin analysis described by the authors in two previous papers,[3] in which it was shown that the methods adopted as official both here and abroad are greatly in error, exceeding 200 per cent in some cases. Changing a method of analysis upon which millions of dollars of tanning materials are bought and sold annually is admittedly a serious matter. Were the new method to supplant the old in the sale of extracts, drastic price changes would have to be made and many extracts would no longer hold their present relative standings or reputation as to tanning value. Since the official methods have been clearly proved unreliable, it would seem that the new method must now be tested generally to determine whether or not it will meet all the conditions that ought to be required of a method so important. Until now its use has been restricted because the procedure as originally described was both cumbersome and time consuming, all of the first efforts having been directed exclusively to devising an accurate method. But the procedure has since been developed until it is now quite as simple as that of any method in general use. In this paper we describe the simplified procedure, and also refute the objections which have been raised against the new method.

DEFINITION OF TANNIN

A thorough review of the literature shows that it has been generally agreed to class as tannin that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. Much confusion would have been avoided in discussion by making it clear whether the criticism was directed against the definition or the method.

CHANGES IN PROCEDURE

In the method as originally described, the tanned hide powder had to be washed by shaking with water for 30 min., squeezing through linen, and repeating with fresh water until free from soluble matter, which usually required about twelve washings. This is now accomplished with very little effort in a washing apparatus to be described later. The washed powder, after drying, was analyzed for water, ash, fat, and hide substance (N$\times$5.62), and the percentages of these subtracted from 100 gave the per cent of tannin in the powder. It was suggested earlier that this figure might be obtained simply by noting the increase in weight of the dry powder after tanning and washing, provided the washing operation were so conducted that no powder was lost, making the determination direct instead of by difference and increasing the accuracy for unskilled analysts. The new washing apparatus not only makes this possible, but reduces the amount of hide powder required for a determination to one-sixth.

PRESENT PROCEDURE

A solution of the tanning material is prepared of such

[1] Received July 26, 1921.

[2] To be presented before the Leather Chemistry Section at the 62nd Meeting of the American Chemical Society, New York City, September 6 to 10, 1921.

[3] THIS JOURNAL, 12 (1920), 465, 1149.

strength that 2 g. of hide powder will detannize 100 cc. in 6 hrs. of shaking. With a little experimenting, safe limits are easily determined for all ordinary materials so that the need for repetition will be rare. For the extracts used in this work, suitable concentrations in grams per liter are 20 for hemlock, larch, oak, and sumac, 16 for gambier, and 7 for solid quebracho. The solution must be freed from insoluble matter, which may be done in the usual manner by adding kaolin, filtering through a thin paper, returning the filtrate to the paper for an hour to tan it, then discarding all liquor which has touched the paper, pouring fresh liquor on to the filter and collecting when the filtrate comes through clear. For materials which filter with difficulty, time can be saved by setting up several filters at one time. Standard hide powder,[1] or its equivalent, is extracted with chloroform to remove all extractable matter, and is then freed from solvent and stored ready for use. This treatment is chiefly to remove fatty matters, and it may be found convenient to treat a year's supply at once. Two grams of this powder, of known moisture content, are put into a 6-oz., wide-mouth bottle, 100 cc. of tan liquor are added, and the whole is put into a rotating box and shaken for 6 hrs. It is advisable to keep the liquor and wash water cool to guard against any tendency towards decomposition of the untanned portion of the hide powder. This matter requires attention only in hot weather.

The essential part of the washing apparatus is shown in Fig. 1 and consists of three glass parts fitting tightly into one another by means of ground joints. A small piece of fine filter cloth is stretched tightly over the bottom outlet of part B and is firmly secured by winding and tying strong thread around the groove. Parts B and C are then put together and the stopcock is opened. The tan liquor and hide powder, after the 6-hr. shaking, are washed into part B, the liquor being allowed to run through the open cock into a beaker and returned until reasonably clear.[2] The stopcock is then closed and B is half filled with water and then fitted to part A with stopcock closed.

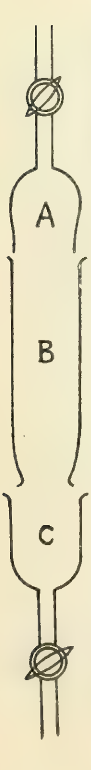


Fig. 1—Glass Washing Apparatus for Use in Wilson-Kern Method of Tannin Analysis or in Determination of Water-Soluble Matter in Leather. Scale 1:4.

The remaining part of the washing apparatus is a reservoir of water set high enough from the table to exert a pressure equal to a column of about 4 ft. of water upon the glass receptacle, which is connected to the reservoir by means of a rubber tube attached to A. The stopcock in A is opened wide, and the rate of flow of water is regulated to about 500 cc. per hr. by means of the stopcock in C, which is connected to the drain. Since the washing is usually complete in about 12 hrs., it is convenient to start it just before leaving the laboratory in the evening so that it will be complete at the start of the next day. However, washing should not be stopped until the wash water is colorless and does not darken upon the addition of a drop of ferric chloride.

The powder is then washed on to a Büchner funnel and freed from as much water as possible by suction. It is then allowed to dry in the air over night, after which it is completely dried in a vacuum oven for 2 hrs., desiccated and weighed. It is returned to the oven and reweighed as a check against insufficient drying. The increase in weight of the dry powder represents the amount of tannin present in 100 cc. of the original tan liquor.

We have found it very convenient to have rotating boxes capable of holding twelve bottles each and cylindrical stands equipped with twelve washing devices each. Given twelve filtered liquors Monday morning, the powders would be tanned and ready for washing before evening, ready for drying next morning, and the tannin values available before noon Wednesday. With one such outfit an analyst can easily complete twelve determinations every day and still have time for other work.

COMPARATIVE ANALYSES

The analyses of six typical extracts given in Table I show that there is practically no difference in results obtained by the original and revised procedures of the new method. Analyses by the official method of the American Leather Chemists Association, widely used in this country, are given for comparison.

TABLE I—COMPARATIVE ANALYSIS OF EXTRACTS BY A. L. C. A. METHOD AND THE ORIGINAL AND REVISED PROCEDURES OF THE NEW METHOD

	A. L. C. A. METHOD				NEW METHOD	
					Tannin	
EXTRACT	Water	Insoluble	Nontannin	Tannin (By Difference)	Original Procedure (By Difference)	Revised Procedure (Direct)
Gambier	48.84	7.58	15.78	27.80	7.32	7.44
Hemlock	51.76	7.32	15.04	25.88	16.38	16.39
Larch	51.63	5.41	20.00	22.96	12.70	12.82
Oak	53.51	2.55	18.35	25.59	11.63	11.42
Quebracho	19.41	9.50	6.86	64.23	44.33	44.03
Sumac	49.44	2.86	22.56	25.14	13.10	13.04

DISCUSSION

A common objection to the new method has been that it appeared inconceivable that leather chemists everywhere should have been so misguided as to accept as official a method liable to a 200 per cent error. The fallacy in the argument put forward lies in its assumption that leather chemists everywhere have found the official methods to be borne out quantitatively in practice. When data were called for to prove this assumption, apparently none were available. On the contrary, we have been able to secure data from both upper and sole leather yards showing that the amount of tannin appearing in the finished leather is very much less than entered the yards according to the A. L. C. A. method, and that the apparent loss of tannin corresponds closely to the difference in tannin content of the extracts as determined by the new and official methods.

After some experimenting with the new method, Schultz and Blackadder[1] raised a number of objections to it. Their first was that it was difficult to obtain concordant results, which they explained as being due in part to the fact that the tannin was determined by difference and was subject to the errors involved in determining the water, ash, fat, and hide substance in the tanned powder. This appears to us rather a matter of skill in manipulation, but in any event the cause has vanished with the revision of the procedure.

Their second objection was that the detannized liquor and wash waters gave a test for tannin when concentrated to small bulk. In an earlier paper[2] we showed that certain nontannins are converted into tannin when their solutions are evaporated and that this transformation can be followed by means of the new method, but not by the A. L. C. A. method.

---

[1] Prepared by the Standard Mfg. Co., Ridgway, Pa.

[2] This liquor must always be tested for tannin by adding, one drop at a time, a freshly prepared solution of 10 g. gelatin and 100 g. sodium chloride per liter. A precipitate indicates that tannin is present, in which case the determination must be repeated, using a more dilute solution of the tanning material.

[1] *J. Am. Leather Chem. Assoc.*, 15 (1920), 654.

[2] THIS JOURNAL, 12 (1920), 1119.

Their third objection was that the degree of subdivision of standard hide powder is not uniform, that the finer portions become more heavily tanned but are more easily lost during the washing operation or in later handling, thus tending to give low results for tannin as a result of making the analyses on the portions of powder less heavily tanned. In the revised procedure no loss of powder during the washing is possible, and all of the powder is weighed after drying. It is worthy of note, however, that the results we obtained by the original and revised procedures are practically identical.

Schell[1] has raised an objection to the method that involves the definition of tannin. Following the work of Meunier,[2] he conceives the existence of two kinds of tannin which may be likened to quinone and hydroquinol. Meunier showed that quinone has tanning properties, while hydroquinol apparently has none. Given plenty of access to the air, however, solutions of hydroquinol become capable of tanning because of oxidation. According to Schell, the new method determines only the quinone-like tannin and fails to include hydroquinol-like bodies.

But hydroquinol admittedly has no tanning properties. It seems to us that the method is all the more accurate for not including as tannin, those bodies which are not tannin, although convertible by oxidation or otherwise into tannin. The existence of these substances in tanning materials has been recognized and discussed in our last paper, in which it was shown that the tannin content of a tan liquor is increased by boiling. There is good reason to believe that the new method can be developed to determine the amount of substances convertible into tannin as well as of actual tannin. This might be done simply by analyzing the liquor both before and after some special treatment, such as oxidation, that will convert into tannin all substances capable of such conversion. However, the data available to us indicate that only a fraction of these substances really appear as tannin in the finished leather.

Schell is right in insisting that these nontannins have a value which should be recognized in judging the value of an extract, but the values should be recognized also of those substances which aid in the diffusion of the tannins into the hides and the sugars which form the necessary acids. Two extracts of apparently the same tannin content may have very different properties. The tannin content alone is no sure guide to the value of an extract; much importance is attached to the reputation of the extract manufacturer. It is not improbable that it will eventually be found preferable to sell extracts on a basis of total solid matter, leaving the extract men to compete with each other in establishing a reputation for producing extracts of high quality and constant composition.

In speaking of hydroquinol-like bodies, Schell implies the suggestion that what the official method really determines is the sum of these and the true tannins, but this is not so. Gallic acid belongs to the class of nontannins capable of conversion into tannin, but when added to a tan liquor only a variable fraction of it appears as tannin by the A. L. C. A. method, which makes the method quite unreliable and often very misleading. This is strikingly shown with gambier extract. The method calls for 12.5 g. of dry hide powder to detannize 200 cc. of tan liquor, which amount was assumed to be correct because the nontannin filtrate gave no test with the gelatin-salt reagent. Using this method on a gambier extract we found 26 per cent tannin. But we then reduced the amount of hide powder to 1.5 g.; the nontannin filtrate gave a negative test with the gelatin-salt reagent, but the per cent of tannin found was only 13. The extract is listed as containing 26 per cent tannin simply because a group of men were more favorably disposed to make 12.5 g. of hide powder official than some other amount. This is treated more fully in our first paper.

The A. L. C. A. method is based upon a principle often employed in adsorption experiments. It falsely assumes that the decrease in concentration of a tan liquor upon shaking with hide powder is a measure of the tannin content and that the solution absorbed by the substance of the hide is of the same composition as the remaining liquor. Thomas and Kelly[1] have shown to what ridiculous conclusions this can lead. In studying the effect of concentration of chrome liquor upon the adsorption of its constituents by hide substance, they had occasion to use very strong liquors. Hide powder was treated with a chrome liquor containing 14.75 g. of chromic oxide per liter, but after 48 hrs. the concentration had *risen* to 15.40 g., although the hide powder had actually removed chromium from solution. This would correspond to a negative value for tannin by the A. L. C. A. method. What happened was that the hide powder absorbed a solution more dilute than the remaining chrome liquor and therefore concentrated the liquor more than enough to offset the chromium removed by combination with the hide substance. It is quite clear that one cannot determine the amount of matter removed from solution by noting the decrease in concentration of the liquor and calculating according to the instructions of the A. L. C. A. method.

SYNTHETIC TANNINS

A representative of a firm manufacturing synthetic tanning materials of the Neradol type informed us that the use of the official method on their product meant nothing as it could be made to give any results desired. He was anxious to learn if the new method would indicate the per cent of matter capable of forming a stable compound with hide substance. While we have done no work with syntans, as they are called, it is obvious that they differ from ordinary tan liquors in that they usually contain a large amount of free sulfuric acid. In using the new method on such materials there is the possibility that the acid might cause the hide substance to swell considerably during washing. This would slow down the washing action and tend to favor decomposition of hide substance, with a consequent loss in accuracy of the method. It seems possible that this might be avoided by using tap water saturated with salt for the first washings, until all sulfuric acid was removed, and then completing the washing with distilled water.

SUMMARY

A modification of the authors' new method of tannin analysis is described which results in a great saving of time and labor, and tends towards increased accuracy.

Objections raised against the new method are refuted.

It is shown that the principle underlying the present official methods is unsound.

A suggestion for using the new method with snytans is made.

According to the Interstate Commerce Commission's figures, chemicals and explosives furnished railroads in the country 17,336,161 tons of freight during the calendar year 1920. Fertilizers furnished 13,976,256 tons during the same period, these commodities together furnishing 1.39 per cent of the total tonnage carried by the railroads in 1920.

---

[1] *Le Cuir*, **9** (1920), 491.

[2] *Chimie & industrie*, **1** (1918), 71.

[1] THIS JOURNAL, **13** (1921), 31.

The Preparation of Ethylene by Hydrogenation of Acetylene[1,2]

By William H. Ross, James B. Culbertson and J. P. Parsons

Chemical Laboratory, Edgewood Arsenal, Edgewood, Maryland

The earliest work on the hydrogenation of acetylene was done by Sabatier and Senderens during the course of their general investigations on the hydrogenation of organic compounds by catalysis.[3] It was observed that when one volume of acetylene and three volumes of hydrogen were passed through a tube containing reduced nickel the temperature rose to 100° to 150°, and the recovered gas consisted almost entirely of ethane and hydrogen. When the proportion of hydrogen was reduced to two volumes, the recovered gas consisted of 5.3 per cent acetylene, 15.0 per cent ethylene, and 79.1 per cent ethane. On reducing the proportion of hydrogen still further, the nickel became hotter, aromatic hydrocarbons were formed, and the recovered gas analyzed as follows: acetylene, 23.0 per cent, ethylene 18.3 per cent, ethane 61.0 per cent, and hydrogen 2.5 per cent.[4]

A similar result was obtained with platinum, but at the same temperature this catalyst is slower in its action.[5] Reduced copper at temperatures of 150° or above also acts as a catalyst in bringing about the combination of hydrogen and acetylene to form ethylene mixed with other hydrocarbons. It was found, however, that when the mixture contained half its volume of acetylene the reaction was attended by the formation of cuprene and that this metal was therefore less promising than nickel for the hydrogenation of acetylene.[6]

Paal and his co-workers found that combination of hydrogen and acetylene occurs when a mixture of these gases is shaken with a colloidal solution of platinum or palladium in water.[7]. Using equal volumes of the gases mentioned, there was recovered in this way a gas which analyzed 80 per cent ethylene.[8]

The reaction between the gases in this process is a relatively slow one, however, and when an excess of hydrogen is used ethane is formed, as in the case of nickel catalyst.

The present paper describes experiments that were undertaken to increase the yield of ethylene in the hydrogenation of acetylene by means of nickel.

Preparation of Nickel Catalyst

The catalyst was prepared from pure nickel nitrate, according to the method of Sabatier and Espil.[9] The oxide prepared from the nitrate was reduced to metallic nickel with hydrogen in the apparatus represented in Fig. 1. In order to remove the last traces of moisture and of oxygen from the hydrogen it was passed through sulfuric acid in the wash bottle E, over copper gauze, G, heated to redness in the electric furnace F_1, and finally over sticks, H, of solid potassium hydroxide. At this point the flow of hydrogen was divided and directed into teach of four tubes, I, containing the nickel oxide to be reduced. The tubes were placed in an electric furnace, F_2, and during he reduction were maintained at a temperature of 300°, as indicated by a thermometer placed in one of the tubes. The reduction of the oxide to metallic nickel was assumed to be complete when the moisture which first formed on the walls of the tubes leading to the absorption traps had completely disappeared. When the furnaces were shut off for the night or at the end of the reduction, the outlets of the traps J were closed, the hydrogen cylinder was shut off, and in its place there was joined in with the apparatus by means of the 3-way stopcock the reservoir of hydrogen, D. In this way the catalyst could be cooled in hydrogen without any decrease in pressure occurring in the tubes.

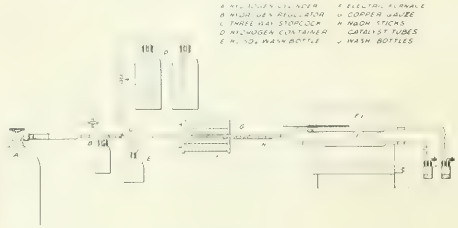


FIG. 1

Each tube in which the nickel oxide was reduced was about 30 cm. long and 2 cm. in diameter, and was sealed at each end to a coarse capillary tube about 10 cm. long. The nickel oxide was placed in the tube after one of the capillary tubes had been sealed on. The quantity of oxide taken amounted to about 20 g., sufficient to fill the tube about one-third full. This was spread out in a train covering the whole length of the tube when placed horizontally. Metallic nickel deposited on 20-mesh pumice was also used.

Apparatus and Method

In testing out the action of nickel catalyst on mixtures of hydrogen and acetylene use was made of the apparatus represented in Fig. 2. The two gases were measured and mixed in the graduated gas buret C, of 300-cc. capacity. The tube containing the reduced nickel is represented at G in the figure. F is a manometer in connection with the tube, and H is a graduated receiver in which the gases could be collected over mercury after passing through or over the catalyst.

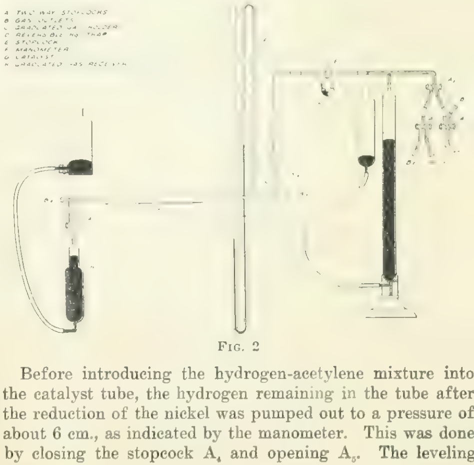


FIG. 2

Before introducing the hydrogen-acetylene mixture into the catalyst tube, the hydrogen remaining in the tube after the reduction of the nickel was pumped out to a pressure of about 6 cm., as indicated by the manometer. This was done by closing the stopcock A_4 and opening A_5. The leveling bottle of the receiver H was then lowered so as to create a

---

[1] Received June 15, 1921.

[2] Published by permission of the Director of the Chemical Warfare Service.

[3] Paul Sabatier, "La catalyse en chimie organique."

[4] *Compt. rend.*, **128** (1899), 1173.

[5] *Compt. rend.*, **131** (1900), 40.

[6] *Compt. rend.*, **130** (1900), 1559.

[7] *Ber.*, **48** (1915), 275, 1195, 1202.

[8] *Chem.-Ztg.*, **36** (1912), 60.

[9] *Compt. rend.*, **158** (1914), 668.

decrease in pressure within the catalyst tube. The gas withdrawn into H was discharged through the outlet B_4, and the process was repeated if necessary until the desired vacuum was obtained.

By cautiously turning stopcock A_4 the gaseous mixture from the buret C could be passed over the catalyst at any desired rate, as indicated by the mercury trap D; or by opening stopcocks E and A_4 the mixture could be passed quickly into the catalyst tube to normal pressure and left in contact with the catalyst as long as desired. This latter procedure was followed in most of the experiments.

When equal parts of hydrogen and acetylene combine to form ethylene a reduction in volume occurs to one-half of the original mixture, while a still greater decrease in volume occurs if the reaction proceeds to paraffin formation. Any reaction which takes place when a mixture of hydrogen and acetylene is quickly passed to normal pressure into an evacuated catalyst tube will therefore be indicated when connected with the apparatus of Fig. 1 by a rise of the mercury in the manometer F. The time taken for the mercury to rise any given height will likewise indicate the rapidity at which the reaction takes place. With an active catalyst at room temperature and in a tube holding about 75 cc. of free gas, the column of mercury in the manometer after adding a mixture of equal volumes of hydrogen and acetylene was often observed to rise to a height of 38 cm. in 1.5 min. With an inactive catalyst, on the other hand, no change took place in the level of the mercury.

ADSORPTION OF HYDROGEN

At the end of the first day's experiments the hydrogen-acetylene mixture that had been in contact with the catalyst was pumped out, and hydrogen was added to normal pressure, with a view to decreasing the danger of any leak into the apparatus while standing over night. Instead of the pressure remaining constant as was expected, the manometer indicated almost as great a degree of exhaustion within the tube as before the hydrogen was added. A similar result was also observed, but to a less marked extent, when acetylene was passed into an evacuated tube that had previously contained hydrogen. However, when a tube containing freshly reduced nickel was exhausted in the same way and hydrogen was introduced again, no decrease in pressure occurred.

These results could be explained if active nickel has the power of adsorbing an appreciable amount of hydrogen or acetylene, which is retained on the surface of the finely divided metal after the free gas within the tube had been pumped out. Experiments were accordingly undertaken to measure the extent of such adsorption of hydrogen, acetylene, and ethylene as occurred in the catalyst used in the experiments. This work has not yet been completed, but the preliminary results indicate that at ordinary temperature hydrogen is adsorbed in active nickel to a considerably greater extent than in coconut charcoal.[1]

The fact being established that the active nickel used in these experiments contained adsorbed hydrogen, a further study was made of its action by exhausting a tube containing active catalyst and then quickly passing in acetylene alone to normal pressure. Reaction at once took place, as indicated by a rapid rise of the mercury in the manometer. The tube was then pumped out as before, and acetylene was again added. On repeating this treatment a number of times it was found that acetylene could be left in contact with the catalyst indefinitely without any change taking place in its composition. That the catalyst still remained active was shown by pumping out the acetylene and filling the tube with hydrogen. A marked reduction of pressure quickly took place, hydrogen disappeared, and the recovered gas consisted largely of ethane. By repeating the treatment with hydrogen, the acetylene in turn was eliminated and hydrogen could then be left in contact with the catalyst without any reduction in pressure taking place. These results indicate that acetylene will react with the hydrogen adsorbed in nickel catalyst; that the adsorbed hydrogen in an active catalyst can be removed by repeated treatment with acetylene without destroying its activity; that an active catalyst from which the adsorbed hydrogen has been removed has no action on acetylene; and that acetylene as well as hydrogen is adsorbed in active nickel.

MEASUREMENT OF RELATIVE ACTIVITY OF CATALYSTS

These results suggested a simple method of measuring the relative activity of different nickel catalysts by connecting each tube in turn in the apparatus, exhausting to a given pressure, quickly passing in a mixture of equal parts of hydrogen and acetylene to normal pressure, and noting the time taken for the mercury to rise to a given height while the tube was maintained at constant temperature. The activity of the different catalysts was assumed to be proportional to the rate at which the mercury rose in the manometer. Having made these determinations in portions of different catalysts, steps were also taken to determine the adsorbed hydrogen by combustion in the remaining portion of each, with a view to ascertaining if the activity of a catalyst in the hydrogenation of acetylene is proportional to its capacity for adsorbed hydrogen. This work has not yet been completed.

FORMATION OF ETHANE

Since reduced nickel contains adsorbed hydrogen it will follow that a catalyst tube that has been evacuated and filled with a hydrogen-acetylene mixture of equal parts will actually contain an excess of hydrogen over that required for ethylene. Reduction of the latter to ethane would therefore be expected. This was found to be the case in a set of experiments in which a mixture of equal parts of hydrogen and acetylene were passed over a new catalyst at ordinary temperature at the rate of 2 cc. per min. The recovered gas was found to contain only a trace of acetylene, 8.7 per cent of ethylene, and over 80 per cent of paraffins. The experiments were repeated with the reacting tube maintained at a temperature of —10° by surrounding it with a freezing mixture. It was thought that at this temperature the reduction of ethylene to ethane might possibly be diminished or entirely inhibited. At the lower temperature the activity of the catalyst was found to have decreased somewhat. By regulating the flow of the gas, samples were sometimes recovered containing upwards of 50 per cent ethylene, but in every case a considerable percentage of ethane was also present. Mixtures of equal volumes of ethylene and hydrogen were substituted for the acetylene-hydrogen mixtures and passed over the catalyst at the same temperature as before. It was found that when the flow of the gas was sufficiently reduced almost complete conversion into ethane took place. This shows that ethylene as well as acetylene will undergo hydrogenation at a temperature as low as —10°.

Since there is a reduction in volume to one-half when equal parts of hydrogen and acetylene combine to form ethylene while the decrease in volume is still greater if the reaction proceeds to paraffin formation, it was thought that possibly the pressure of the gases in the catalyst tube might

---

[1] Cf. L. Troost and P. Hautefeuille, *Compt. rend.*, 80 (1875), 788; G. P. Baxter, *Am. Chem. J.*, 22 (1899), 351; Adolf Sieverts, *Z. physik. Chem.* 60 (1907), 129; 77 (1911), 591; M. Mayer and V. Altmayer, *Ber.*, 41 (1908), 3062; G. Neuman and F. Streintz, *Monatsh.* 12 (1891), 642; T. W. Richards and A. S. Cushman, *Proc. Am. Acad.*, 34 (1899), 333.

TABLE I.—PERCENTAGE COMPOSITION OF COMPOSITE SAMPLES OF GAS COLLECTED WHEN MIXTURES OF HYDROGEN AND ACETYLENE WERE PASSED OVER NICKEL CATALYST.

	A		B		C		D		E		F		G	
Component	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered
Ethylene, C_2H_4	...	66.8	...	71.1	...	73.0	...	74.7	...	77.8	...	81.5	...	82.2
Acetylene, C_2H_2	41.7	0.0	48.4	8.9	48.2	11.0	49.4	13.1	48.8	9.1	45.2	0.6	47.4	1.1
Ethane, C_2H_6	...	16.3	...	10.6	...	3.6	...	6.6	...	7.1	...	11.9	...	8.6
Hydrogen, H	55.3	1.0	49.1	3.5	49.6	0.4	49.3	0.0	49.9	0.3	53.5	0.0	51.3	0.6
Oxygen, O	0.4	2.8	0.4	0.7	0.4	0.3	0.2	0.5	0.2	0.5	0.2	0.6	0.2	0.4
Nitrogen, etc. (by difference)	2.6	13.1	2.1	5.2	1.8	11.7	1.1	5.1	1.1	5.2	1.1	5.4	1.1	7.1

have some effect on the reaction as suggested by Le Chatelier's principle. The experiments were accordingly repeated by passing the gaseous mixture over the catalyst at room temperature but at different pressures below normal. It was not noticed, however, that the change in pressure, which was varied from normal to one-twelfth of an atmosphere, had any appreciable effect, under the conditions of the experiment, in decreasing the proportion of ethane formed.

YIELD OF ETHYLENE

The experiments were repeated with a freshly reduced catalyst from which all adsorbed hydrogen was removed by repeated treatment with acetylene. The tube was then exhausted, and equal volumes of hydrogen and acetylene were passed in quickly to normal pressure and allowed to remain until the pressure decreased to half an atmosphere. The resulting gas was then pumped out and analyzed. By this treatment there was obtained a marked increase in the percentage of ethylene formed. Results of analyses of composite samples collected over several days are given in Table I.

From the results given in Table I it is seen that a comparatively small variation in the proportion of hydrogen to acetylene in the mixture taken produces a marked change in the composition of the recovered gas. Best results seem to be attained when the hydrogen in the mixture is slightly in excess of the acetylene. A further increase in the proportion of hydrogen, however, results in a decrease of ethylene with a corresponding increase of ethane. When a considerable excess of acetylene is taken, no hydrogen is found in the recovered gas and very little ethane. In a series of experiments in which the proportion of acetylene to hydrogen in the mixture varied up to two parts of the former to one of the latter it was found that the acetylene and ethylene in the recovered gas amounted to 91.5 per cent. The impurities in the gas which came from that occurring in the original mixture amounted to 5.4 per cent, which leaves a total of only 3.1 per cent for the ethane and other constituents which make up the balance of the gas.

The acetylene used in these experiments was obtained from an ordinary acetylene cylinder. An analysis of the gas at the beginning of the experiments showed 94.7 per cent of acetylene which later increased to 96.4 per cent, and finally to 98.1 per cent. The purity of the hydrogen amounted to 99.3 per cent. If one volume of hydrogen were to combine with one volume of acetylene to give one volume of ethylene, then the impurities in the product, which owe their source to that occurring in the original mixture, would amount at first to 6.0 per cent, and with the gases finally used, to 2.6 per cent. The excess of the nonabsorbable and noncombustible components found in the recovered gas, over what was to be expected from the impurities in the original mixture, was no doubt due to a slight leak of air through the stopcock A_5 (Fig. 2) as the apparatus was being pumped out.

To determine if any slight decomposition of acetylene occurs when in contact with active nickel, an analysis was made for carbon and hydrogen in a catalyst that had been in almost constant use for a period of several weeks. Mixtures of equal parts of hydrogen and acetylene were passed over the nickel before being taken from the tube. The analysis as determined by combustion showed the presence in the nickel of 1.09 per cent of carbon and 0.41 per cent of hydrogen by weight. The ratio of hydrogen to carbon in the sample was therefore even greater than that corresponding to methane. If the carbon occurred in the sample analyzed in the free state, then the hydrogen would have a volume under standard conditions of about 400 cc. per unit volume of the nickel. This is greatly in excess of the quantity found adsorbed in a freshly prepared catalyst. It must therefore be concluded that no appreciable amount of carbon was deposited on the nickel and that the carbon and hydrogen found owe their source to free hydrogen and to hydrocarbons which are either adsorbed in, or deposited on, the nickel.

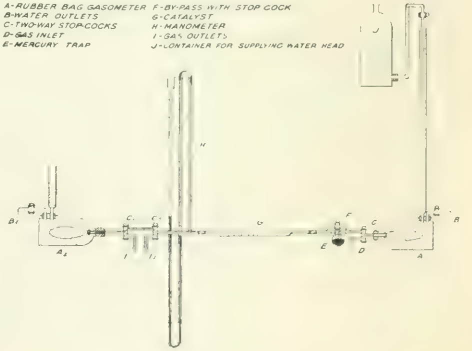


Fig. 3

LARGE SCALE APPARATUS

In order to collect larger quantities of ethylene than could conveniently be done with the equipment shown in Fig. 2, use was made of a second apparatus as represented in Fig. 3. The hydrogen and acetylene mixture was stored in the rubber bag of the gasometer A_1, of 2000-cc. capacity. By means of the pressure supplied by the head of water in the aspirator bottle J, the gas in the bag could be passed at any rate through the stopcock C_1, the mercury trap E, and the catalyst G, and be collected in the bag of the gasometer A_2. The water of this gasometer was displaced through B_2. The rate at which the gas was passed over the catalyst could be roughly measured by counting the bubbles per second passing through E. On an average each bubble had a volume of 0.06 cc. To remove the adsorbed hydrogen from a freshly prepared catalyst, the tube in which it was contained was evacuated through the outlet I_2, after closing C_1 and opening C_3. The latter stopcock was then closed, and the pressure within the tube was brought to normal again by passing in a portion of the hydrogen-acetylene mixture from A_1 through the by-pass F. When the mercury rose to a constant height in the manometer the gas was again pumped out, and the process was repeated until the composition of the recovered gas became constant. The same mixture was now passed slowly at practically normal pressure over the catalyst, and the product of the reaction was collected in the gasometer A_2. With an arrangement of this kind the reaction could be allowed to proceed at night, as the flow of water from J automatically stopped when the bag in the gasometer A_1 became empty.

Sample A, Table I, represents the average of several samples collected while the rubber bag of the gasometer A_2 was suspended in the air. The analysis would seem to indicate that a slight exchange of gas had taken place through the walls of the bag. Sample B represents the mean of several collected with the bag in the gasometer as shown.

METHODS OF ANALYSIS

In the preliminary experiments described in the early part of this work, use was made of the Tucker and Moody method for determining ethylene in the presence of acetylene.[1] This method consists in passing the gases through an ammoniacal silver nitrate solution, which is claimed to remove the acetylene completely, but only a relatively small amount of ethylene. It was found, however, that the quantity of ethylene absorbed so varied with different conditions, particularly with the time the mixture was shaken with the silver nitrate solution, as to make the method impractical for determining the degree to which the composition of the recovered gas was affected by any modification in the conditions of the experiment.

Tests were made with a method developed during the course of this work by Ross and Trumbull,[2] of this laboratory. This method, which is based on the volumetric determination of the nitric acid set free when acetylene is precipitated with excess of silver nitrate solution, was found to be rapid, accurate, and simple of manipulation, and it therefore greatly facilitated the progress of this investigation. In the analysis of samples containing ethylene, as well as acetylene, the percentage of the former present was taken as the difference between the total percentage absorption in fuming sulfuric acid and the value obtained for the percentage of acetylene in the sample. For the determination of the other components in the sample analyzed use was made of the usual methods of gas analysis as described in Dennis' "Gas Analysis."

EXPERIMENTS WITH FILCHAR AS CATALYST

Since charcoal is known to act as a catalytic agent in bringing about reactions between different gases, as for example in the combination of carbon monoxide and chlorine to make phosgene, it was thought advisable to test any effect which the material might have on the hydrogenation of acetylene. The material selected for the experiments consisted of screened filchar of medium-sized grains. This was placed in a Pyrex glass tube similar to that used in the experiments with nickel catalyst. The tube was heated to 700°, and chlorine was passed through until the charcoal had undergone complete chlorination and all tarry matter present in the pores of the material had been destroyed. Nitrogen was then passed through the tube at the same temperature as before, followed by enough hydrogen to drive out the nitrogen, after which the tube was allowed to cool down in an atmosphere of hydrogen. The tube containing the filchar was then placed in an apparatus similar to that represented in Fig. 2. The gas was pumped out to 6 cm. of mercury, and a mixture of hydrogen and acetylene in equal volumes was added at normal temperature. After standing for several hours the rise of mercury in the manometer amounted to only a few millimeters. At 50° and even at 100° the rise of mercury was still less than at normal temperature. This shows, as was also confirmed by an analysis of the gas, that under the conditions of the experiment filchar is without action in bringing about the combination of hydrogen and acetylene.

ACKNOWLEDGMENT

This investigation was suggested by Major Wm. L. Evans, in charge of the Chemical Laboratory of Edgewood Arsenal at that time, and the authors wish gratefully to acknowledge the courtesy and kind assistance which was tendered them at all times during the course of this work.

SUMMARY

Metallic nickel reduced from the oxide at 300° has a greater capacity than coconut charcoal for adsorbing hydrogen at ordinary temperature. When a mixture of equal volumes of hydrogen and acetylene is passed into an evacuated tube about one-third filled with freshly reduced nickel, the hydrogen adsorbed in the nickel, together with that added, may be sufficient to bring about the complete reduction of the acetylene to ethane. By repeating the process of evacuating the tube and passing in the hydrogen-acetylene mixture until the excess of hydrogen is used up, a product may be obtained which contains upward of 80 per cent of ethylene. A comparatively small variation in the composition of the mixture taken produces a considerable change in the composition of the recovered gas. Best results seem to be obtained when the hydrogen in the mixture is slightly in excess, but as this is further increased the ethylene decreases, with corresponding increase of ethane. As the acetylene in the mixture is increased the ethane in the product decreases, and the sum of the ethylene and acetylene increases.

The adsorbed hydrogen in an active nickel catalyst may be eliminated without destroying its activity by repeated treatment with acetylene. The catalyst is then without action on either ethylene or acetylene.

A simple apparatus is described for measuring the relative activities of different nickel catalysts.

VULCANIZATION OF RUBBER

A new method for the vulcanization of rubber is described in a recent article by Professor Bruni of the Pirelli Research Laboratories, Milan, Italy. He states that if certain accelerators such as thiocarbanilide which are formed by the action of an organic amine and carbon bisulfide are produced relatively to the rubber in the nascent state, particularly in the presence of zinc oxide, curing takes place at ordinary temperatures.

---

[1] *J. Am. Chem. Soc.*, 23 (1901), 671; see also Dennis, "Gas Analysis," p. 249.

[2] *J. Am. Chem. Soc.*, 41 (1919), 1180.

Viscosity-Temperature Curves of Fractions of Typical American Crude Oils[1,2]

By **E. W. Dean** and **F. W. Lane**

Bureau of Mines, Petroleum Division, Chemical Section, Pittsburgh, Pa.

Published information regarding the variation of the viscosity of petroleum oils with temperature is, according to the observations of the authors, notably inadequate. Relatively few data are available in print, and in all cases there is a decided absence of information regarding the origin and history of the samples on which tests were made. The investigation reported in the present paper was undertaken by the Bureau of Mines for the purpose of obtaining figures showing the viscosity-temperature relationships of a reasonably wide range of petroleum fractions of known origin and of accurately determined physical properties.

SCOPE AND GENERAL METHOD OF PROCEDURE

The following three crude oils were selected for the present series of tests:

1—A sample of Pennsylvania crude petroleum obtained from a small refinery located in Pittsburgh, Pa. This oil was regarded as representative of the so-called "paraffin base" class.

2—A sample of crude petroleum from the Sunset Field, Kern County, Cal., which was regarded as representative of the class of so-called "naphthene base" oils.

3—A sample of crude petroleum from the Salt Creek Field, Natrona County, Wyo., which was regarded as representative of the class of so-called "intermediate base" oils.

Analyses of these samples according to the Bureau of Mines procedure for crude oil appear in Table I.

The viscosity determinations recorded in subsequent tables were made on fractions distilling at atmospheric pressure between limits of 100° to 125° C. (212° to 257° F.) 125° to 150° C. (257° to 302° F.), etc., up to 250° to 275° C. (482° to 527° F.), and on all the "vacuum" fractions. These fractions are designated hereafter by letters and numbers indicating the crude from which they were derived, the pressure under which they were distilled, and the upper (centigrade) distillation limit. Thus, for example, "W-V-250" represents a fraction from Wyoming crude, separated between limits of 225° to 250° C. (437° to 482° F.) in the "vacuum" distillation at 40 mm.; "C-A-175" indicates a fraction from California crude, distilling between 150° and 175° C. (302° to 347° F.) at atmospheric pressure, etc.

Viscosity determinations were made at the following temperatures: 0° C., 10° C., 20° C., 30° C., 40° C., 50° C., 60° C., 80° C., and 100° C. (32° F., 50° F., 68° F., 86° F., 104° F., 122° F., 140° F., 176° F., and 212° F.). For obvious reasons, tests were not made at all points on all fractions; some of the fractions distilling at atmospheric pressure have excessive vapor pressures at 80° C. and 100° C., and some of the "vacuum" fractions solidify partly or totally at temperatures as high as 30° C.

The determinations of viscosity-temperature curves for distillation fractions were supplemented by tests on the following oils: (1) The residuum (designated as "P-R") from the distillation of the Pennsylvania crude, (2) a mixture (designated as "P-mixt") of this residuum and the Pennsylvania fraction "P-V-225," and (3) a mixture (designated as "P-C-mixt") of "P-R" and the California fraction "C-V-250."

Results in terms of kinematic viscosity (absolute viscosity divided by density) are given in full. Saybolt Universal equivalents are given for the majority of figures representing kinematic viscosities in excess of 0.0142 (32 sec., Saybolt Universal). Transformations were made by the use of the Bureau of Standards equation[1]

$$V_k = 0.00220\, t_s - \frac{1.80}{t_s}$$

in which V_k is kinematic viscosity and t_s Saybolt Universal viscosity.

TABLE I—RESULTS OF ROUTINE ANALYSES OF SAMPLES OF CRUDE PETROLEUM FROM WHICH WERE OBTAINED THE FRACTIONS USED FOR VISCOSITY-TEMPERATURE MEASUREMENTS

SAMPLE No. 640

Pennsylvania

Specific gravity—0.809 Baumé gravity—43.1°

Per cent sulfur—0.16 Per cent water—Nil

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Air distillation, first drop, 24°C. (75°F.)

Temperature °C.	Per cent Cut	Sum Per Cent	Sp. gr. Cut	Bé Cut	Viscosity[1]	Cloud Test °F.	Temperature °F.
Up to 50	1.5	1.5	0.639	89.1			Up to 122
50– 75	2.8	4.3	0.662	81.5			122-167
75–100	3.3	7.6	0.702	69.4			167–212
100–125	7.2	14.8	0.728	62.3			212–257
125–150	6.0	20.8	0.746	57.7			257–302
150–175	6.5	27.3	0.760	54.2			302–347
175–200	5.5	32.8	0.773	51.1			347–392
200–225	6.5	39.3	0.785	48.3			392–437
225–250	5.9	45.2	0.797	45.7			437–482
250–275	7.0	52.2	0.810	42.8			482–527
Vacuum distillation at 40mm.							
Up to 200	4.6	4.6	0.829	38.9	39.1	16	Up to 392
200–225	5.2	9.8	0.834	37.9	44.5	36	392–437
225–250	5.2	15.0	0.842	36.3	53.5	55	437–482
250–275	5.2	20.2	0.850	34.7	71.2	74	482–527
275–300	6.0	26.2	0.859	33.0	109.5	90	527–572
Residuum			0.894	26.6	726.8		Residuum

Carbon residue of residuum—2.3 per cent

SAMPLE No. 474

California Sunset Field Kern County

Specific gravity—0.878 Baumé gravity—29.5°

Per cent sulfur—0.73 Per cent water—Nil

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Air distillation, first drop—26C°. (79°F.)

Temperature °C.	Per cent Cut	Sum Per cent	Sp. gr. Cut	°Bé Cut[1]	Viscosity	Cloud Test °F.	Temperature °F
75–100	1.3	1.3	0.742	58.7			167–212
100–125	3.9	5.2	0.761	54.0			212–257
125–150	4.5	9.7	0.782	49.0			257–302
150–175	4.0	13.7	0.805	43.9			302–347
175–200	3.7	17.4	0.818	41.1			347–392
200–225	4.8	22.2	0.844	35.9			392–437
225–250	5.5	27.7	0.860	32.8			437–482
250–275	5.9	33.6	0.874	30.2			482–527
Vacuum distillation at 40mm.							
Up to 200	3.6	3.6	0.891	27.1	42.5		Up to 392
200-225	4.8	8.4	0.904	24.9	53.8		392–437
225-250	4.9	13.3	0.917	22.7	89.4		437–482
250-275	5.3	18.6	0.932	20.2	203.1		482–527
275-300	8.3	26.9	0.942	18.6	427.3		527–572

Carbon residue of residuum—16.4 per cent

SAMPLE No. 561

Wyoming Salt Creek Field Natrona County

Specific gravity—0.841 Baumé gravity—36.5°

Per cent sulfur—0.18 Per cent water—Nil

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Air distillation, first drop—25°C. (77°F.)

Temperature °C.	Per cent Cut	Sum Per cent	Sp. gr. Cut	°Be. Cut	Viscosity[1]	Cloud Test °F.	Temperature °F
Up to 50	1.4	1.4	0.669	79.3			Up to 122
50– 75	1.8	3.2					122-167
75–100	4.5	7.7	0.716	65.5			167-212
100–125	6.7	14.4	0.744	58.2			212–257
125–150	5.1	19.5	0.764	53.2			257–302
150–175	5.8	25.3	0.783	48.8			302-347
175–200	4.0	29.3	0.797	45.7			347–392
200–225	4.4	33.7	0.810	42.8			392–437
225–250	5.4	39.1	0.822	40.3			437-482
250–275	6.3	45.4	0.833	38.1			482–527
Vacuum distillation at 40mm.							
Up to 200	4.1	4.1	0.849	34.9	40.1	19	Up to 392
200–225	6.1	10.2	0.852	34.3	45.2	39	392–437
225–250	6.1	16.3	0.860	32.8	57.6	63	437–482
250–275	5.6	21.9	0.865	31.9	80.2	77	482–527
275–300	5.4	27.3	0.874	30.2	130.8	90	527–572

Carbon residue of residuum—6.1 per cent

[1] Viscosity figures are Saybolt Universal sec., at 100°F.

EXPERIMENTAL

The distillation methods used for preparing the various fractions are to be described in full in Bureau of Mines *Bulletin* 207, which will be published at a slightly later date. The method involves distilling a 300-cc. charge of oil in a special glass flask, equipped with a 6-in. Hempel column, until a vapor temperature of 275° C. (527° F.) is reached. The flask and its contents are then allowed to cool. The Hempel column is removed and replaced by a "spray catching" device consisting of three inverted gauze cones. The flask is attached to a properly designed "vacuum" system, and the distillation is continued at a reduced pressure of 40 mm. absolute until a vapor temperature of 300° C. (572° F.) is reached. Fractions are separated at temperature limits that are multiples of 25° C. (The respective Fahrenheit limits are 45° apart.)

---

[1] Presented before the Section of Petroleum Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[1] W. H. Herschel, "Standardization of the Saybolt Universal viscosimeter," Bureau of Standards, *Technologic Paper* 112 (1919), 2d ed., 19.

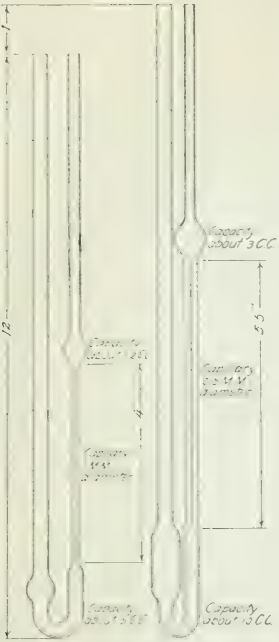


Fig. 1 Form and approximate dimensions of two extremes of set of Ostwald viscosimeters used in present series of experiments

Viscosity determinations were made by means of specially constructed Ostwald viscosimeters, about a dozen of which were used. These instruments varied somewhat in the size of the upper bulb and the length and bore of the capillary. The approximate dimensions of two extremes of the set are shown in Fig. 1. Viscosimeters having relatively large bulbs and long, fine capillaries were, of course, used for the less viscous fractions, whereas for viscous oils the small-bulbed instruments with shorter, wider capillaries were more convenient.

METHOD OF FILLING VISCOSIMETERS—The problem of filling viscosimeters offered a little difficulty, as the conventional procedure of introducing a known volume of liquid from a pipet is obviously unsatisfactory in the case of the more viscous fractions. The scheme finally adopted involved using the lower reservoir of the viscosimeter as a measuring container. The process of filling was accomplished by setting up a viscosimeter in a vertical position and introducing oil through the wider arm by means of a pipet or pressure injector equipped with a long, slender tip. The oil was run in "drop-wise" after the reservoir had become approximately three-quarters full and the flow was stopped as soon as the level of the liquid reached the junction of the capillary and the reservoir. This point was indicated very accurately by a "shooting up" when the oil first entered the capillary.

STANDARDIZATION OF VISCOSIMETERS—Each viscosimeter was standardized by determining the efflux time with each of at least two liquids of known viscosity, the "known" liquids being distilled water, and samples of oil for which kinematic viscosity figures were supplied by the Bureau of Standards. The selection of calibrating liquids was determined by the "rapidity" or "slowness" of the viscosimeter under test. For the "slower" instruments, that is, the ones with large bulbs and long, fine capillaries, water and one of the less viscous "standard" oils were used. The more "rapid" viscosimeters were standardized with two oil samples. The method of standardization involved the assumption of the following relationship:

$$V_k = At \qquad (1)$$

in which V_k is kinematic viscosity, t the efflux time and A a constant characteristic of the viscosimeter. The general equation is

$$V_k = At - \frac{B}{t} \qquad (2)$$

in which the term $\frac{B}{t}$ (the kinetic energy correction) is negligible if the rate of flow of liquid through the capillary is sufficiently slow. The employment of two liquids in the standardization of each viscosimeter indicated the negligible magnitude of the "kinetic energy correction" for when two liquids of differing viscosity give the same value for A in Equation 1 it is obvious that neither of them flows with sufficient rapidity to necessitate the use of Equation 2.

THE "FILLING FACTOR"—In case a viscosimeter is filled at one temperature and the efflux time is determined at some other temperature, it is obvious that some sort of a correction factor must be employed to compensate for the change in "head" brought about by thermal expansion or contraction of the oil. For purposes of operating convenience the authors usually filled viscosimeters at temperatures of either 25° C. (77° F.) or 100° C. (212° F.). Actual determinations of viscosity were, of course, made at temperatures ranging from 0° C. (32° F.) to 100° C. (212° F.). It was necessary, therefore, to use a series of so-called filling factors to compensate for the errors that would otherwise have been introduced by this detail of procedure. An average factor was determined for the whole set of instruments by making viscosity tests on certain oils at 100° C. (212° F.) with filling temperatures of 25° C. (77° F.) and 100° C. (212° F.). The average ratio for this difference in filling temperature was 1.023 at 100° C. Using this figure as a basis, the set of "filling factors" given in Table II was calculated.

TABLE II—FILLING FACTORS USED WHEN VISCOSIMETERS ARE FILLED AT 25° C. (77° F.) OR 100° C. (212° F.) AND VISCOSITY DETERMINATIONS MADE AT OTHER TEMPERATURES

Temperature at which Viscosity Determination is Made		"Filling Factor" when Pipet is Filled at 25° C. (77° F.)	"Filling Factor" when Pipet is Filled at 100° C. (212° F.)
°C.	°F.		
0	32	0.992	....
10	50	0.995	...
20	68	0.999	...
30	86	1.002	0.979
40	104	1.005	0.982
50	122	1.008	0.985
60	140	1.011	0.988
70	158	1.014	0.991
80	176	1.017	0.994
100	212	1.023	1.000

The equation actually used for the calculation of results therefore takes the form:

$$Vk = Atf \qquad (3)$$

in which V_k is kinematic viscosity, A the constant characteristic of the viscosimeter used, and f a properly selected filling factor from Table II.

It should perhaps be stated that the authors recognize the fact that their method of standardization and calculation involves certain approximations that would not be justifiable if the highest possible degree of precision were necessary. It has seemed, however, that the consumption of time necessary for increased accuracy is greater than is warranted through any possible advantage that could be gained.

MISCELLANEOUS OPERATING DETAILS—Actual determinations were made with the viscosimeters immersed in constant temperature baths. A vigorously stirred mixture of cracked ice and distilled water gave a temperature of 0° C. (32° F.), while temperatures from 10° C. (50° F.) to 70° C.

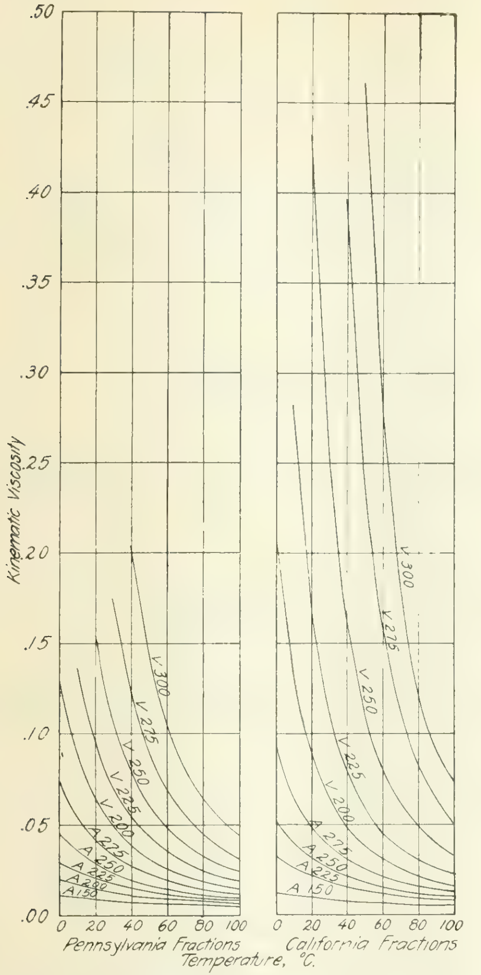


Fig. 2—Viscosity-temperature curves of sets of distillation fractions derived from Pennsylvania and California crude petroleum

(158° F.) were maintained by the use of water baths equipped with the conventional devices for thermostatic control. The baths for 80° C. (176° F.) and 100° C. (212° F.) consisted of glass jackets through which benzene vapor and steam were passed. Both of these baths were maintained under pressures so regulated as to give the precise temperatures desired.

At least three determinations of the efflux time were made for each oil at each temperature, and the viscosity figures reported were calculated from the mean of these experimental values.

Discussion of Results

The calculated figures for the kinematic viscosities are given in Table III. Table IV shows equivalent Saybolt Universal figures for the "vacuum" fractions, the Pennsylvania residuum and the two mixtures previously referred to.

Fig. 2 shows graphically the majority of the data included in Table III, *A* and *B*, and indicates the similarities and differences of the viscosity-temperature curves for fractions from two extreme types of crude oil. It will be observed that the curves representing low boiling ranges and low viscosities are not unlike, but that there are impressive differences in the "higher" fractions. The curves for the California oil are much steeper than those for Pennsylvania cuts and indicate a greater variation of viscosity with temperature. Curves for the Wyoming oil are not shown. They have characteristics intermediate between those of the Pennsylvania and California curves and resemble the former more closely than they do the latter.

While it is felt that the method of plotting the results adopted in Fig. 2 is the most effective way of illustrating the points emphasized above, another scheme of graphic representation has certain advantages.[1] If the reciprocals of the kinematic viscosities as ordinates are plotted against the temperatures as abscissas, the resulting lines are straight for the lighter fractions, and only slightly curved for the heavier fractions. A plot so constructed permits easier interpolation than the type of diagram shown in Fig. 2. For the gasoline fractions, a straight line drawn through two experimental points will represent satisfactorily the viscosity temperature relationship while for the heavier oils, three or more points obviously will be required to determine the curve. This subject is considered from a mathematical standpoint in a later connection.

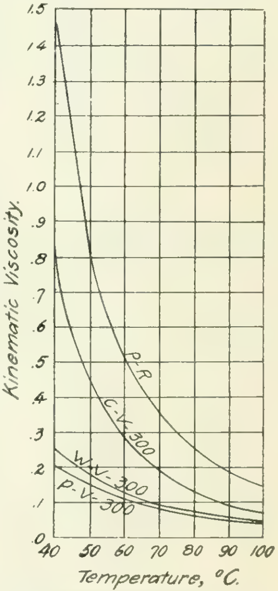


Fig. 3—Viscosity-temperature curves of several of the more viscous products derived from Pennsylvania, California and Wyoming crude petroleum.

Fig. 3 shows in detail a comparison of curves characteristic of viscous oils derived from Pennsylvania and California crude petroleums. The upper curve, marked "P-R" represents the residuum from the combined "air" and "vacuum" distillations of the Pennsylvania crude. This residuum is a product the properties of which approach those of so-called steam cylinder stock. Its viscosity is high throughout the entire range of temperature, but it belongs to the same family as the lowest two curves of the diagram, marked "W-V-300" and "P-V-300," and representing respectively vacuum distillation fractions cut between limits of 275° to 300° C. (527° to 572° F.) from the Wyoming and Pennsylvania crudes. The intermediate curve, marked "C-V-300," representing the highest vacuum fraction from the California crude, shows at 100° C. (212° F.) a viscosity slightly higher

---

[1] The authors are indebted to Professor Robert E. Wilson, of the Massachusetts Institute of Technology, for bringing to their attention the practical advantages of this method.

TABLE III—KINEMATIC VISCOSITIES AT VARIOUS TEMPERATURES OF A SERIES OF PRODUCTS DERIVED FROM CRUDE PETROLEUM

Designation of Product	Description of Product: Pressure under which Distilled	Temperature Limits of Cut °C.	°F.	Kinematic Viscosities Determined at Indicated Temperatures: 0° C. 32° F.	10° C. 50° F.	20° C. 68° F.	30° C. 86° F.	40° C. 104° F.	50° C. 122° F.	60° C. 140° F.	80° C. 176° F.	100° C. 212° F.	Kinematic Viscosities Calculated or Interpolated for Indicated Temperatures: 37.8° C. 100° F.	54.4° C. 130° F.	98.9° C. 210° F.
							A—Pennsylvania Crude								
P-A-125	Atmospheric	100–125	212–257	0.00880	0.00780	0.00703	0.00643	0.00593	0.00542	0.00508	0.00456				
P-A-150	Atmospheric	125–150	257–302	0.0111	0.00957	0.00869	0.00780	0.00708	0.00649	0.00603	0.00524	0.00467			
P-A-175	Atmospheric	150–175	302–347	0.0141	0.0121	0.0106	0.00946	0.00849	0.00769	0.00702	0.00618	0.00548			
P-A-200	Atmospheric	175–200	347–392	0.0199	0.0166	0.0142	0.0123	0.0110	0.00964	0.00871	0.00737	0.00642			
P-A-225	Atmospheric	200–225	392–437	0.0298	0.0236	0.0196	0.0167	0.0145	0.0127	0.0112	0.00926	0.00781			
P-A-250	Atmospheric	225–250	437–482	0.0454	0.0345	0.0277	0.0227	0.0191	0.0164	0.0143	0.0115	0.00958			
P-A-275	Atmospheric	250–275	482–527	0.0729	0.0529	0.0407	0.0322	0.0265	0.0221	0.0188	0.0147	0.0120			
P-V-200	40-mm. vac.	175–200	347–392	0.1296	0.0884	0.0642	0.0489	0.0384	0.0315	0.0259	0.0195	0.0152	0.0400	0.0289	0.0153
P-V-225	40-mm. vac.	200–225	392–437	......	0.1372	0.0962	0.0704	0.0544	0.0432	0.0356	0.0247	0.0186	0.0574	0.0394	0.0188
P-V-250	40-mm. vac.	225–250	437–482			0.1533	0.1079	0.0798	0.0609	0.0484	0.0327	0.0238	0.0841	0.0546	0.0242
P-V-275	40-mm. vac.	250–275	482–527	......			0.1746	0.1225	0.0899	0.0694	0.0448	0.0312	0.1314	0.0797	0.0318
P-V-300	40-mm. vac.	275–300	527–572	......			......	0.2044	0.1444	0.1064	0.0654	0.0441	0.2245	0.1248	0.0450
P-R	Residuum						......	1.498	0.8064	0.5248	0.2581	0.1468	1.596	0.6780	0.1512
P-Mixt.	Mixture residuum and fraction P-V-225							0.1669	0.1208	0.0918	0.0570	0.0396			
							B—California Crude								
C-A-125	Atmospheric	100–125	212–257	0.0103	0.00902	0.00807	0.00735	0.00665	0.00610	0.00565	0.00488	......			
C-A-150	Atmospheric	125–150	257–302	0.0124	0.0108	0.00957	0.00860	0.00775	0.00711	0.00661	0.00570	0.00505			
C-A-175	Atmospheric	150–175	302–347	0.0162	0.0138	0.0120	0.0106	0.00942	0.00847	0.00773	0.00651	0.00568			
C-A-200	Atmospheric	175–200	347–392	0.0223	0.0185	0.0158	0.0135	0.0119	0.0105	0.00943	0.00781	0.00673			
C-A-225	Atmospheric	200–225	392–437	0.0332	0.0263	0.0215	0.0180	0.0154	0.0134	0.0120	0.00961	0.00817			
C-A-250	Atmospheric	225–250	437–482	0.0523	0.0396	0.0312	0.0252	0.0210	0.0179	0.0154	0.0121	0.00987			
C-A-275	Atmospheric	250–275	482–527	0.0935	0.0656	0.0486	0.0375	0.0302	0.0249	0.0209	0.0158	0.0124			
C-V-200	40-mm. vac.	175–200	347–392	0.2142	0.1328	0.0902	0.0645	0.0485	0.0383	0.0308	0.0217	0.0165	0.0510	0.0348	0.0166
C-V-225	40-mm. vac.	200–225	392–437	......	0.2825	0.1717	0.1136	0.0803	0.0596	0.0459	0.0303	0.0219	0.0848	0.0529	0.0222
C-V-250	40-mm. vac.	225–250	437–482	......	0.8393	0.4360	0.2548	0.1628	0.1122	0.0807	0.0482	0.0322	0.1766	0.0962	0.0328
C-V-275	40-mm. vac.	250–275	482–527	...			0.6926	0.3877	0.2372	0.1572	0.0825	0.0502	0.4380	0.1961	0.0514
C-V-300	40-mm. vac.	275–300	527–572	.				0.8282	0.4612	0.2836	0.1305	0.0736	0.9363	0.3686	0.0757
P-C-Mixt.	Mixture of Pennsylvania residue and C-V-250			..				0.3228	0.2108	0.1465	0.0811	0.0517			
							C—Wyoming Crude								
W-A-125	Atmospheric	100–125	212–257	0.00927	0.00829	0.00741	0.00675	0.00609	0.00567	0.00533					
W-A-150	Atmospheric	125–150	257–302	0.01141	0.00999	0.00890	0.00803	0.00730	0.00669	0.00622	0.00547	0.00489			
W-A-175	Atmospheric	150–175	302–347	0.0151	0.0129	0.0113	0.0100	0.00895	0.00808	0.00752	0.00628	0.00547			
W-A-200	Atmospheric	175–200	347–392	0.0207	0.0173	0.0148	0.0128	0.0114	0.0101	0.00907	0.00760	0.00646			
W-A-225	Atmospheric	200–225	392–437	0.0299	0.0241	0.0200	0.0169	0.0146	0.0127	0.0114	0.00919	0.00773			
W-A-250	Atmospheric	225–250	437–482	0.0452	0.0348	0.0281	0.0231	0.0193	0.0165	0.0143	0.0114	0.00935			
W-A-275	Atmospheric	250–275	482–527	0.0737	0.0542	0.0414	0.0327	0.0268	0.0224	0.0191	0.0146	0.0116			
W-V-200	40-mm. vac.	175–200	347–392	0.1432	0.0976	0.0698	0.0526	0.0412	0.0330	0.0274	0.0199	0.0155	0.0433	0.0303	0.0157
W-V-225	40-mm. vac.	200–225	392–437		0.1491	0.1026	0.0743	0.0563	0.0442	0.0356	0.0251	0.0188	0.0596	0.0401	0.0101
W-V-250	40-mm. vac.	225–250	437–482		......	0.1792	0.1227	0.0892	0.0672	0.0528	0.0356	0.0257	0.0955	0.0600	0.0260
W-V-275	40-mm. vac.	250–275	482–527				0.2070	0.1418	0.1033	0.0774	0.0483	0.0334	0.154	0.0905	0.0340
W-V-300	40-mm. vac.	275–300	527–572					0.2501	0.1701	0.1230	0.0723	0.0470	0.274	0.146	0.0480

TABLE IV—SAYBOLT UNIVERSAL VISCOSITIES AT VARIOUS TEMPERATURES OF A SERIES OF PRODUCTS FROM CRUDE PETROLEUM
(Fractions distilled at 40-mm. vacuum)

Designation of Fraction	Temperature Limits of Fraction °C.	°F.	Saybolt Viscosities: 0°C. 32°F.	10°C. 50°F.	20°C. 68°F.	30°C. 86°F.	40°C. 104°F.	50°C. 122°F.	60°C. 140°F.	80°C. 176°F.	100°C. 212°F.	37.8°C. 100°F.	54.4°C. 130°F.	98.9°C. 210°F.
							A—Pennsylvania Crude							
P-V-200........	175–200	347–392	70.5	55.0	46.7	41.8	38.6	36.6	35.1	33.4	32.3	39.1	35.9	32.3
P-V-225........	200–225	392–437		73.5	57.9	48.8	43.5	40.1	37.8	34.8	33.1	44.5	38.9	33.2
P-V-250........	225–250	437–482		. .	79.9	62.2	52.0	45.6	41.7	37.0	34.5	53.5	43.6	34.6
P-V-275........	250–275	482–527				88.6	67.8	55.6	48.4	40.5	36.6	71.2	52.0	36.7
P-V-300........	275–300	527–572					101.0	76.4	61.6	47.1	40.3	109.5	68.7	40.6
P-R............	Residuum						682.2	368.8	241.6	123.9	77.3	726.8	310.8	79.1
P-Mixt	Mixture P-R and P-V-225						85.5	67.1	56.2	44.3	39.0			
							B—California Crude							
C-V-200...... ..	175–200	347–392	105.1	71.8	55.7	46.8	41.7	38.6	36.4	33.9	32.6	42.5	37.6	32.6
C-V-225...... ..	200–225	392–437	.	134.5	87.4	64.3	52.2	45.2	40.9	36.3	34.0	53.8	43.1	34.1
C-V-250...... ..	225–250	437–482		383.5	202.2	122.5	83.8	63.8	52.3	41.6	36.8	89.4	57.9	37.0
C-V-275...... ..	250–275	482–527	.			317.5	180.7	114.9	81.5	53.0	42.2	203.1	97.5	42.6
C-V-300...... ..	275–300	527–572	.				378.7	213.5	135.0	70.8	49.9	427.5	172.3	50.6
P-C-Mixt..... ..	Mixture P-R and C-V-250		.				152.1	103.7	77.2	52.5	42.8			
							C—Wyoming Crude							
W-V-200..... ..	175–200	347–392	75.9	58.4	48.6	43.0	39.5	37.1	35.5	33.5	32.3	40.1	36.3	32.4
W-V-225..... ..	200–225	392–437		78.3	60.2	50.1	44.2	40.3	37.8	34.8	33.3	45.2	39.1	33.3
W-V-250..... ..	225–250	437–482	.	.	90.5	67.8	55.3	47.6	43.0	37.8	35.0	57.6	45.3	35.1
W-V-275 ..	250–275	482–527		.		102.1	75.3	60.5	51.2	41.6	37.2	80.2	55.8	37.4
W-V-300..... ..	275–300	527–572					120.5	86.7	68.0	49.4	41.2	130.8	77.0	41.5

than those of the corresponding Pennsylvania and Wyoming products, whereas at the lower temperatures it approaches more closely the viscosity of the Pennsylvania residuum.

Fig. 4 shows viscosity-temperature curves for typical kerosene fractions ("P-A-225," "C-A-225," and "W-A-225") from the Pennsylvania, California, and Wyoming crudes. Viscosity differences are of the same type as those shown for higher boiling, more viscous fractions, but are of a lesser order of magnitude.

Fig. 5 gives interesting indications regarding the viscosity-temperature curves of mixtures. It has just been pointed out (refer to Fig. 3) that the viscosity-temperature curve of the Pennsylvania residuum resembles the curves for the distillates from the same crude. In Fig 5 the curve marked "P-mixt" represents a blend of Pennsylvania residuum and the Pennsylvania vacuum fraction "P-V-225." It will be noted that this curve is entirely similar to those obtained from the fractions "P-V-300" and "P-V-275," between which it lies. The curve marked "P-C-mixt" represents

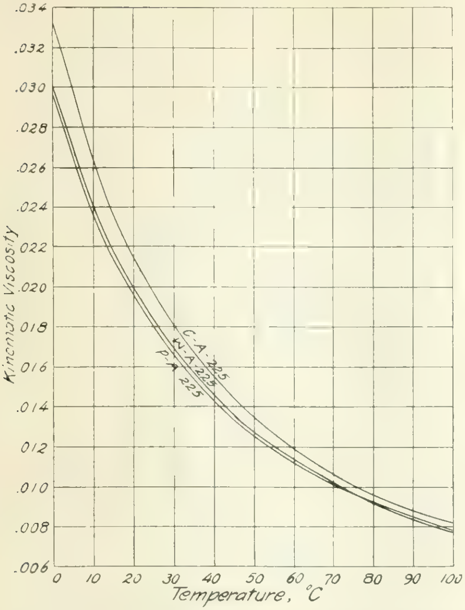


Fig. 4 Viscosity-temperature curves of typical kerosene fractions derived from Pennsylvania, California and Wyoming crude petroleum

a mixture of the Pennsylvania residuum and one of the lighter vacuum fractions of the California crude. It will be noted that its slope is not as steep as that of the adjacent curve "C-V-275," representing a "straight" California distillate.

The indications furnished by these comparisons point to the fact that the viscosity-temperature curves of the important group of commercial lubricating oils made by blending "paraffin base" distillates and "paraffin base" residuums show the same characteristics as the corresponding curves for "straight" distillates. When blends are composed of oils derived from different types of crude petroleum the characteristics of the curves are intermediate between those of the constituents.

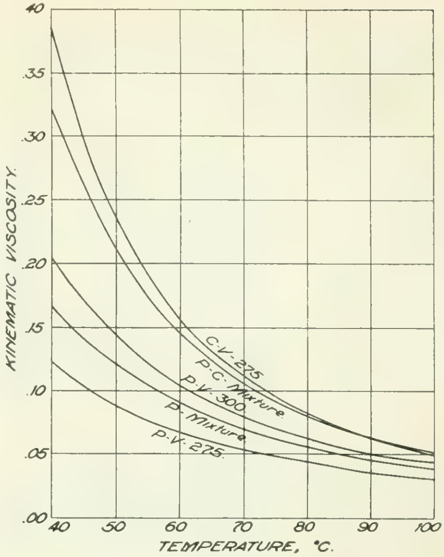


Fig. 5—Showing that the viscosity-temperature curve of a mixture of Pennsylvania distillate and Pennsylvania residuum has the same form as curves for unblended Pennsylvania distillates, whereas the curve for a mixture of California distillate and Pennsylvania residuum varies appreciably from the form of a curve for unblended California distillate.

General Characteristics of Viscosity-Temperature Curves

From the data presented in Tables III and IV, and in Figs. 2 to 5, inclusive, two conclusions may be drawn. In the first place, the work done apparently indicates the nonexistence of any simple rule by means of which the variation of viscosity with temperature can be predicted. The ratio between viscosities at different temperatures varies with the type of crude petroleum from which the oil is derived and also with the physical and chemical properties of fractions from a given crude. For example the kinematic viscosity at 100° C. (212° F.) of the California fraction "C-V-300" is 8.9 per cent of the figure determined for 40° C. (104° F.). A corresponding ratio for the Pennsylvania fraction "P-V-300" is 21.6 per cent. It may be noted further that for the Pennsylvania fraction "P-V-250" the ratio between kinematic viscosities at the same two temperature points is 29.8 per cent. Similar variations may be discovered when comparisons are made of products derived from different crudes and having equal viscosities at any given temperature. This matter is discussed in more detail in a later connection.

Table V—Values of the Calculated Constants K,[1] A and B Representing the Viscosity Temperature Curves of the Distillation Fractions Derived from Pennsylvania and California Crude Petroleum

Temperature Limits of Fraction °C	F°.	Pressure under which Distilled	Pennsylvania Fractions K	A	B	California Fractions K	A	B
100–125	212–257	Atmospheric	113.2	1.498	—0.00200	97.60	1.287	+0.000688
125–150	257–302	Atmospheric	90.19	1.300	0.000591	80.74	1.204	—0.000298
150–175	302–347	Atmospheric	70.30	1.250	—0.00126	61.32	1.108	+0.000450
175–200	347–392	Atmospheric	49.60	1.072	—0.0000380	44.14	0.989	+0.000623
200–225	392–437	Atmospheric	33.50	0.865	+0.000794	29.57	0.853	0.000813
225–250	437–482	Atmospheric	21.37	0.751	+0.000840	18.61	0.661	0.00169
250–275	482–527	Atmospheric	12.97	0.583	0.00130	10.29	0.488	0.00217
175–200	347–392	40-mm vacuum	7.21	0.400	0.00189	4.242	0.309	0.00259
200–225	392–437	40-mm vacuum	4.45	0.252	0.00243	1.254	+0.178	0.00269
225–250	437–482	40-mm vacuum	1.88	0.182	0.00219	0.550	+0.0319	0.00274
250–275	482–527	40-mm vacuum	+0.810	0.0994	0.00213	1.070	—0.0629	0.00252
275–300	527–572	40-mm vacuum	—0.070	0.0522	0.00175	1.967	—0.109	0.00225
Residuum			+0.881	—0.0468	+0.00106			

[1] The viscosity temperature curves can be represented in terms of an equation of the general form

$$V_k = \frac{1}{K + At + Bt^2}$$

in which V_k is kinematic viscosity, t the centigrade temperature and K, A, and B constants characteristic of each individual fraction from each oil.

---

1 Compare Basler chemische Fabrik, D. R. P. 205,377, and 211,696.

Secondly, an outstanding similarity is found in the general form of the various viscosity-temperature curves. These can be represented by equations of the form:

$$V_k = \frac{1}{K + At + Bt^2} \qquad (4)$$

in which V_k is kinematic viscosity, t the centigrade temperature and K, A and B, constants characteristic of each individual fraction from each crude.[1] The values of the constants for the products derived from the Pennsylvania and California crudes have been calculated by the method of least squares and are shown in Table V. The excellent agreement between experimental and calculated values is illustrated by Table VI, which includes figures for several typical fractions.

TABLE VI—AGREEMENT BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF KINEMATIC VISCOSITY OF SELECTED FRACTIONS FROM PENNSYLVANIA AND CALIFORNIA CRUDE PETROLEUM

Temperature °C.	Fraction A-150 Kinematic Viscosity Exp.	Fraction A-150 Kinematic Viscosity Calc.	Fraction A-275 Kinematic Viscosity Exp.	Fraction A-275 Kinematic Viscosity Calc.	Fraction V-225 Kinematic Viscosity Exp.	Fraction V-225 Kinematic Viscosity Calc.	Fraction V-300 Kinematic Viscosity Exp.	Fraction V-300 Kinematic Viscosity Calc.
			Pennsylvania Fractions					
0	0.0111	0.0111	0.0729	0.0771	....	....	....	....
10	0.00957	0.00970	0.0529	0.0528	0.1327	0.1386	....	....
20	0.00869	0.00862	0.0407	0.0398	0.0962	0.0956	....	....
30	0.00780	0.00777	0.0322	0.0316	0.0704	0.0708	....	....
40	0.00708	0.00708	0.0265	0.0261	0.0544	0.0543	0.2044	0.2048
50	0.00649	0.00651	0.0221	0.0220	0.0432	0.0433	0.1444	0.1433
60	0.00603	0.00602	0.0188	0.0190	0.0356	0.0353	0.1064	0.1061
80	0.00524	0.00525	0.0147	0.0147	0.0247	0.0249	0.0654	0.0651
100	0.00467	0.00467	0.0120	0.0119	0.0186	0.0186	0.0441	0.0441
			California Fractions					
0	0.01235	0.01239	0.0935	0.0972	....	....	....	.....
10	0.01080	0.01076	0.0656	0.0650	0.2825	0.3030	....	....
20	0.00957	0.00955	0.0486	0.0478	0.1717	0.1700	....	....
30	0.00860	0.00858	0.0375	0.0372	0.1136	0.1111	....	....
40	0.00775	0.00779	0.0302	0.0300	0.0803	0.0791	0.8282	0.8230
50	0.00711	0.00713	0.0249	0.0249	0.0596	0.0593	0.4612	0.4651
60	0.00661	0.00658	0.0209	0.0211	0.0459	0.0463	0.2836	0.2826
80	0.00570	0.00571	0.0158	0.0158	0.0303	0.0306	0.1305	0.1306
100	0.00505	0.00505	0.0124	0.0124	0.0219	0.0218	0.0736	0.0735

It will be understood that the constants for the viscosity-temperature equation of any oil can be calculated from the experimentally determined viscosities at three suitable temperatures. The method of calculation involves the solution of three simultaneous equations, and does not require the use of the more accurate but decidedly tedious method of least squares.

Obviously, the values for the constants are useful in calculating viscosities at temperatures, within the experimental range, for which actual determinations are lacking. The reliability of such calculated viscosities can be accepted without question; but the use of the constants at temperatures considerably below or above the extremes represented by the experimental data is not to be recommended on account of a possible change in state of the oil, or a change in the viscosity-temperature relationship. While the equations would seem to offer an effective method for estimating solidification temperatures (at which the kinematic viscosity becomes infinite), it is felt that the significance of such calculations is open to question because of the fact that partial solidification so often takes place. In the authors' opinion, it is equally unjustifiable to attempt the calculation of viscosities for temperatures at which the oils have appreciable vapor pressures, and hence are changed in properties through partial distillation.

As an indication of the validity of the equations at temperatures considerably above those covered by the foregoing experimental data, two viscosity determinations were made at approximately 180° C. (356° F.) and compared with the calculated figures based on the experimental range 40° to 100° C. (140° to 212° F.). Table VII (part *A*) shows the agreement to be satisfactory in both cases.

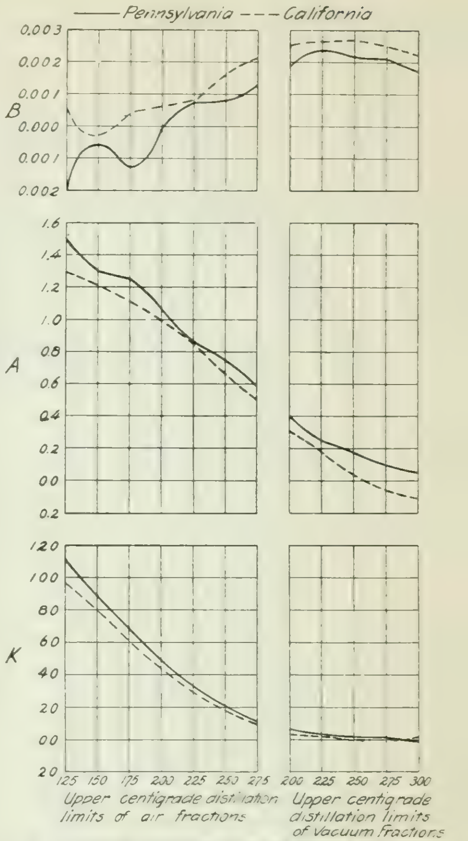


Fig. 6—Showing similarities in curves obtained by plotting against upper distillation limits the values of the constants K, A and B from the equations representing viscosity-temperature curves of the series of fractions from Pennsylvania and California crude petroleum

TABLE VII—CALCULATED AND EXPERIMENTAL VISCOSITY FIGURES FOR RELATIVELY HIGH TEMPERATURES

Part A

PRODUCT	Temperature °C	Kinematic Viscosity Experimental	Kinematic Viscosity Calculated
P-R	181.7	0.0363	0.0366
C-V-300	182.5	0.0171	0.0175

Part B

PRODUCT	Kinematic Viscosity at Temperature Indicated—Experimental 100°C. (212°F.)	Calculated 200°C. (392°F.)	Calculated 300°C. (572°F.)
P-R	0.1468	0.0295	0.0122
P-V-300	0.0441	0.0124	0.00578
C-V-300	0.0736	0.0142	0.00582

Assuming the validity of the equations for temperatures considerably above those of the experimental range, it is interesting to consider the values so calculated as indicating whether viscosity actually becomes constant at higher temperatures. Table VII (part *B*) shows the calculated values at 200° C. (392° F.) and 300° C. (572° F.) as compared with the experimental figures at 100° C. (212° F.). These figures seem to indicate that viscosity continues to decrease even at temperatures as high as 300° C. (572° F.).

The constants for the equations may also possess addi-

---

[1] This is in effect the Slotte equation (See A. E. Dunstan and F. B. Thole "The Viscosity of Liquids," London, **1914**, 4; Schlotte, *Wied. Ann.*, **14** (1881), 13, *Beibl.* 16 (1892), 182; Thorpe and Rodger, *Phil. Trans.*, A, **185** (1894), 397, which is usually employed to indicate the relation between absolute viscosity and temperature but which the authors have found equally useful as applied to kinematic viscosity).

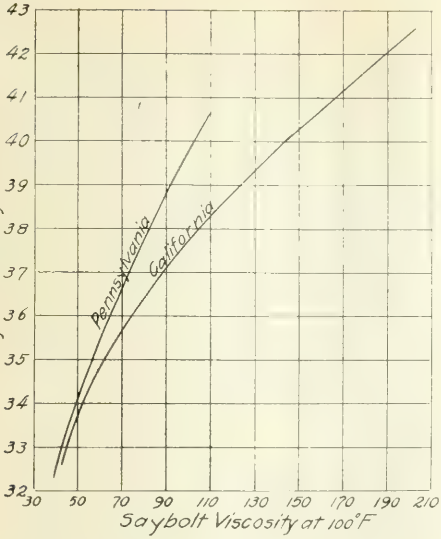


Fig. 7—Showing curves obtained by plotting Saybolt viscosities at 210°F. against aSybolt viscosities at 100°F. for the series of products obtained from Pennsylvania and California crude petroleums.

tional theoretical or practical significance, and the authors have under consideration several possibilities that will be investigated as soon as further experimental data are available. For the present, attention is called only to an interesting relationship indicated by the curves in Fig. 6, which were obtained by plotting values of the constants for the series of fractions from Pennsylvania and California crudes against the upper (centigrade) distillation limit for each cut. An interesting similarity will be noted in the form of the curves representing values of the constants K and A for equivalent fractions from each of the two types of crude petroleum. The similarity becomes equally striking in the curves for the constant B if, instead of adhering so closely to the plotted points as has been done in Fig. 6, more general curves are drawn.

Relation Between Saybolt Viscosities at Different Temperatures

It has already been stated that no simple general rule has been discovered which may be applied to estimate viscosity at one temperature from determinations made at some other temperature.[1] The nearest approach, of practical value, to a relationship of this order is indicated by the fact that a smooth curve may be constructed to represent the viscosities at any two selected temperatures for the series of fractions derived from any given crude. Fig. 7 illustrates this possibility and shows curves obtained by plotting Saybolt Universal viscosities at 210° F. against Saybolt Universal viscosities at 100° F. for the series of products obtained from the Pennsylvania and California crudes. Table VIII includes a series of Saybolt viscosity equivalents for the commonly used temperature points, 100° F., 130° F., and 210° F. This table may prove of practical use in case any oil under consideration is known to be of the same type as either of the two crudes studied by the authors. Such a happy coincidence is, unfortunately, not likely to be a frequent occurrence, and the table is of greatest significance as indicating possibilities of variation when it is attempted to estimate viscosity at one temperature from figures determined at some other temperature. It appears, for example, that Pennsylvania and California products, having at 210° F. a viscosity of 50 sec. Saybolt Universal, have at 100° F. respective viscosities of 209 and 396 sec.

Table VIII—Comparative Saybolt Universal Viscosities at 210°F., 130°F., and 100°F. for Oils Derived from Pennsylvania and California Crude Petroleum

A—Figures for Pennsylvania and California Oils					*B—Figures for Pennsylvania Oils Only*		
Saybolt Viscosity at 210°F.	Saybolt Viscosity at 130°F.		Saybolt Viscosity at 100°F.		Saybolt Viscosity at 210°F.	Saybolt Viscosity at 130°F.	Saybolt Viscosity at 100°F.
	Pa.	Cal.	Pa.	Cal.			
33	37	38	41	42	56	145	291
34	40	41	47	49	57	151	306
35	44	45	53	58	58	157	321
36	48	50	61	69	59	163	337
37	52	56	70	82	60	170	353
38	56	61	79	99	61	176	369
39	60	68	89	119	62	183	385
40	64	74	99	139	63	189	401
41	68	81	109	160	64	195	419
42	73	89	119	181	65	202	437
43	78	97	129	202	66	209	455
44	82	106	139	224	67	216	473
45	87	116	150	249	68	223	491
46	92	125	161	277	69	230	510
47	97	135	172	307	70	237	529
48	102	145	184	337	71	244	548
49	107	154	196	367	72	252	567
50	112	163	209	396	73	259	587
51	117	...	222	422	74	267	...
52	123	...	235	459	75	274	
53	128	...	249	498	76	282	. .
54	134	...	263	537	77	290	. .
55	139	...	277	574	78	299	..
					79	307	...
					80	316	...

It is possible that a proper use of figures for other physical properties of oils might permit reasonably accurate interpolation between limits such as have just been indicated. The data at present available have not, however, seemed adequate to permit formulating any rule for interpolation that would be satisfactorily reliable.

Summary

1—Viscosity-temperature curves have been determined for series of products derived from samples of Pennsylvania, California, and Wyoming crude petroleum.

2—The California fractions show a greater change in viscosity with temperature (the curves are steeper) than the corresponding Pennsylvania products. Differences are most impressive for fractions of high viscosity. Viscosity-temperature curves for the Wyoming fractions show characteristics which are intermediate between those of the California and Pennsylvania curves; but they resemble the latter more closely than they do the former.

3—The viscosity-temperature curve of the undistilled residuum from the Pennsylvania crude is of the same type as the curves for the distillation fractions.

4—The viscosity-temperature curve for a mixture of Pennsylvania residuum and Pennsylvania distillate shows the same characteristics as the curves for unblended distillates. Furthermore, the curve for a mixture of Pennsylvania residuum and California distillate apparently averages the characteristics of the curves of the two constituents.

5—The viscosity-temperature curves for the Pennsylvania, Wyoming, and California kerosene fractions show the same qualitative relationships as those for the lubricating fractions.

6—Viscosity-temperature curves can be represented by an equation of the general form:

$$Vk = \frac{1}{K + At + Bt^2}$$

---

[1] The conclusions of Oelschlager ("The Viscosity of Liquids," *Z. Verein. deut. Ing.*, 62 (1918), 422, *Science Abstracts*, 21-B (1918), 320) are obviously untenable, at least in part, in view of the experimental evidence included in the present paper. The logarithmic relationship developed by this investigator (p. 424) is undoubtedly of considerable value, but his constants are not applicable to lubricating oils from all types of crude petroleum.

Values of the three constants, K, A, and B, have been determined for the products from the Pennsylvania and California crudes. An interesting similarity in form may be noted in the curves obtained by plotting values of these constants against the upper distillation limits of the respective cuts from the two types of crude.

7—Present results have failed to indicate any reliable general method of calculating viscosity-temperature curves of oils for which less than three experimentally determined points are available.

SHORT BIBLIOGRAPHY

Girard. *Mémoires de l'académie des Sciences*, 1816.

Poiseuille. *Recueil des Savants Étrangers* 1842. *Ann. chim. phys.*, [3] 7 (1843), 50.

Couette. "Studies on the Viscosity of Liquids," *Ann. chim. phys.*, [6] 21 (1890), 433.

Thorpe and Rodger. "Relation between the Viscosity of Liquids and Their Chemical Nature," *Phil. Trans.*, A, 185 (1894), 397.

Thorpe and Rodger. "The Viscosity of Mixtures of Miscible Liquids," *J. Chem. Soc.*, 71 (1897), 360.

Beck. "Beitrage zur relativen Innern Reibung," *Z. physik. Chem.*, 58 (1907), 425.

Dunstan and Wilson. "Relation between Molecular Weight and Viscosity of a Series of Compounds," *J. Chem. Soc.*, 91 (1907), 90.

Dunstan and co-workers. "Viscosity of Liquid Mixtures," *J. Chem. Soc.*, 85 (1904), 817; 87 (1905), 11; 91 (1907), 83.

Dunstan and co-workers. "Relation between Viscosity and Chemical Constitution," *J. Chem. Soc.*, 93 (1908), 1919; 95 (1909), 1556.

Findlay. "Viscosity of Binary Mixtures at Their Boiling Points," *Z. physik. Chem.*, 69 (1909), 203.

Bingham. "Viscosity and Fluidity," *Am. Chem. J.*, 35 (1906), 195; 40 (1908), 277; 43 (1910), 287.

Dunstan and Strevens. "The Viscosity of Lubricating Oils," *J. Soc. Chem. Ind.*, 31 (1912), 1063.

Bingham. "Criticism of Some Recent Viscosity Investigations," *J Chem. Soc.*, 103 (1913), 959.

Thole, Mussel and Dunstan. "Viscosity Maxima and Their Interpretation," *J. Chem. Soc.*, 103 (1913), 1108.

Flowers. "Viscosity Measurement and a New Viscosimeter," *Proc. Am. Soc. Test. Materials*, 14 (1914), II, 565.

Anonymous. "Absolute Viscosimeter," *Engineering*, 100 (1915), 554.

Dubrisay. "Method of Testing the Viscosity of Lubricating Oils," *J. Soc. Chem. Ind.*, 36 (1917), 1123.

Herschel. "Determination of Absolute Viscosity by the Saybolt Universal and the Engler Viscosimeters," *Proc. Am. Soc. Test. Materials*, 17 (1917), II,551.

Lidstone. "A Mercurial Viscosimeter," *J. Soc. Chem. Ind.*, 36 (1917), 270, 317.

Sheppard. "The Measurement of the Absolute Viscosity of Very Viscous Media," *J. Ind. Eng. Chem.*, 9 (1917), 523.

Bingham. "Variable Pressure Method for the Measurement of Viscosity," *Proc. Am. Soc. Test. Materials*, 18 (1918), II, 373.

Bingham and Jackson. "Standard Substances for the Calibration of Viscosimeters," Bureau of Standards, *Scientific Paper*, 298.

Dunstan and Thole. "Relation between Viscosity and the Chemical Constitution of Lubricating Oils," *Petroleum Rev.*, 38 (1918), 245, 267.

Herschel. "The Standard Saybolt Universal Viscosimeter," *Proc. Am. Soc. Test. Materials*, 18 (1918), II, 363

Nicolardot and Baume. "The Dubrisay Method of Examining Lubricating Oils" *Analyst*, 43 (1918), 276.

Nicolardot and Baume. "Contribution to the Study of the Viscosity of Lubricating Oils," *Chimie & industrie*, 1 (1918), 265.

Oelschlager. "The Viscosity of Oils," *Z. Ver. deut. Ing.*, 62 (1918), 422.

Thorpe. "Viscosity of Pure Liquids," *Science Progress*, 12 (1918), 583

Faust. "Viscosity Measurements," *Z. physik. Chem.*, 93 (1919), 758.

Herschel. "Standardisation of the Saybolt Universal Viscosimeter," Bureau of Standards *Technolgic Paper* 112 (1919).

Herschel. "Viscosity of Gasoline," Bureau of Standards, *Technolgic Paper* 125 (1919).

Lawaczek. "Viscosity and Its Measurement," *Z. Ver. deut. Ing.*, 63 (1919), 677.

Stanton. "Determination of the Absolute Viscosities of Liquids at High Pressure," *Engineering*, 108 (1919), 520.

Herschel. "The MacMichael Torsion Viscosimeter," *J. Ind. Eng. Chem.*, 12 (1920), 817.

Herschel. "Saybolt Viscosity of Blends," Bureau of Standards, *Technical Paper* 164 (1920).

Schwedhelm. "The Viscosity of Oils and Other Liquids as a Function of the Temperature," *Chem.-Ztg.*, 45 (1921), 41.

The Effect of Chemical Reagents on the Microstructure of Wood[1,2]

By Allen Abrams

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

In connection with research work on paper being carried by this laboratory for the Mead Research Company of Dayton, Ohio, it became desirable to secure an insight into the changes occurring in the structure of wood during various chemical treatments. Consequently, an investigation was undertaken, as a result of which a method was developed and made use of in carrying out such treatments. A number of reagents have been studied, and while the results here presented must be regarded as preliminary and incomplete, it is hoped that they may stimulate further work along similar lines by other investigators.

The most obvious method for studying the effects of reagents on the microstructure of wood would be to treat blocks of the wood with these reagents at the desired temperatures and pressures for specified lengths of time. The wood might then be sectioned and studied either under the microscope or by means of photomicrographs. Unfortunately, however, the mechanical difficulties of sectioning such wood are so great that, even with the most skilful technique, it is apparently impossible to make sections without altering the anatomical structure. For this reason it has been necessary to develop a new procedure, which consists essentially in first making thin sections of wood and treating these with reagents under the proper conditions.

In order that the changes produced by these chemical treatments may be comprehended, it is first desirable to note the three planes in which wood may be sectioned—a *cross* or *transverse* section is one cut perpendicular to the axis of the trunk; a *radial* section is one cut longitudinally along the radius of the trunk; a *tangential* section is one cut longitudinally, tangent to the rings of growth and therefore, perpendicular to the radius of the trunk. Figs. 1, 2, 3 are, respectively, cross, tangential, and radial sections of pine.

CELL STRUCTURE

The process of plant growth is essentially that of cell division whereby each cell in the growing region (the "cambium") is split into two daughter cells. The partition separating these cells is known as the "middle lamella" (Fig. 4). As growth continues, other walls are laid down adjacent to the middle lamella and nearer the hollow interior ("lumen") of the cell.

The complete facts connected with cell growth are extremely complicated. To the paper-maker, however, the important fact is that any chemical process for making paper should have for its primary object the separation of individual cells by dissolving out the middle lamella with as little effect as possible on the remainder of the cell wall. To be sure, another very important action is that of decomposing compound celluloses, such as lignocellulose, and thus producing a pure cellulose.

The history of the cell walls and the study of their chemical structure have been the subjects of extensive research, conducted usually, however, by men with botanical rather than chemical training. The results of these investigations[5] show that the middle lamella should be regarded as the primary partition wall, serving to bind the tracheids together; but at the same time, it must be understood that this layer has a complicated history in which it undergoes changes in form, mass and chemical composition.

Allen[1] is certain that the middle lamella differs chemically from the later walls. He believes that the first formed cellular wall consists essentially of pectin-like substances which are plastic, and therefore undergo such changes in form as are necessary to adapt the layer readily to alterations occurring in the cells during growth. As the cells grow older, the middle lamella becomes more rigid and inflexible, until finally it assumes a hard, insoluble form. This process is believed to consist in a transformation of the pectic acid originally present into an insoluble material, probably calcium pectate.

---

[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Contribution No. 34 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[1] C. E. Allen, *Bot. Gaz.*, 32 (1901), 1.

Aside from the mineral constituents of the cell wall, the most important substances are compounds (probably of an adsorption type) of cellulose, such as lignocelluloses and pectocelluloses. Cross and Bevan[1] compare the lignocellulose structure to an alloy of a base and a noble metal, in which the more reactive base metal may be dissolved out by suitable methods, leaving the comparatively inert noble metal. In a similar way, cellulose is comparatively resistant to the action of reagents such as chlorine, alkalies, or bisulfites, all of which tend to remove the lignin groups. König and Rump,[2] after an extensive chemical and microscopic study, conclude that there are no true compounds of cellulose and other substances in the cell, but that these materials exist here intimately mixed.

Spaulding[3] has made an extensive study of cellulose and lignin in various woods. From this he concludes that, whereas cellulose and lignin are generally intimately mixed in the cell wall, yet in some woods a ring of pure cellulose lines the cell lumen. Moreover, this cellulose is found especially in those cells which do not contain starch, and Spaulding concus with Sablon's[4] previous work on willow, in which Sablon had been led to believe that starch was converted into cellulose.

While there is considerable controversy over the subject, it seems probable that the formation of lignocellulose is a process of thickening by incrustation: colloidal, hydrated celluloses are first formed, and they then take up lignin held in colloidal solution in the sap.[5] These changes follow quite closely upon one another, since heart wood and sap wood give about the same yields of cellulose and lignocellulose.[6]

For the purpose of these considerations, it may then be assumed that the cellular structure is composed largely of intimate mixtures of loose or adsorption compounds of cellulose with lignin and pectin, and the hemicelluloses. The cell walls are largely made up of compounds of lignin and cellulose, while the middle lamella is probably composed largely of pectocelluloses and hemicelluloses.

On account of the fact that these substances are present in a colloidal condition, changes in the individual units cannot be followed by the ordinary microscopic methods. It is only where such changes are expressed in the more extensive structural alterations that the microscope is of value.

Staining with dyes which affect only certain portions of the woody structure has long been the subject of controversy, since some observers advance evidence to show that staining distinguishes mere physical changes in the degree of colloidal dispersion rather than chemical differences in the structure, while other observers take the opposite view. As a matter of fact, it is comparatively unimportant which view we adopt when staining is used in following the changes produced by reagents on a given structure. It is not unreasonable to believe that such chemical and physical changes go hand in hand and that they are both distinguished by staining.

From all the available information it would appear that in cooking wood with various chemicals in aqueous solution, one or more of the following changes is likely to take place:

1—Hydration of the constituents, naturally accompanied by swelling.

2—Depolymerization, or an increase in the degree of colloidal dispersion, of the various woody substances.

Both of these effects are slow and progressive and both are accelerated toward complete peptization or colloidal solution of the constituents as the time, temperature or concentration of the solution is increased.

3—Actual hydrolysis of the constituents, accompanied generally by true solution.

4—Other fairly definite chemical reactions, such as chlorination, oxidation or sulfonation of constituents, followed by colloidal or true solution.

The reagents used in analytical or practical work on cellulose and lignin are naturally chosen because of a more or less selective action on one of these substances. In such cases a knowledge of the changes in microstructure which accompany these reactions should throw some light on what is taking place.

METHOD OF MAKING WOOD SECTIONS

Starting with the tree itself, small blocks of wood (1 in. × 0.5 in . ×0.5 in.) are cut from the portions of the trunk to be studied. These blocks are boiled vigorously in water for about an hour, or until they sink. The air is thus driven out of the tracheids and is replaced by water.

With the Thomson microtome these blocks may be cut at once; but with other microtomes it is generally necessary to soften the blocks several days in cold 50 per cent hydrofluoric acid to dissolve out mineral constituents such as silica. According to Jeffrey,[1] hydrofluoric acid does and attack the middle lamella. On the other hand, its use should be dispensed with wherever possible, as it undoubtedly hydrolyzes some constituents of the wood. (All wood sections used in these experiments were made after acid treatment.)

Following the acid treatment, the block is washed thoroughly in water and is transferred to a mixture of equal parts of ethyl alcohol and glycerol. Sections of from 20 to 40 microns in thickness are made from these blocks. Thinner sections are difficult to handle during later treatments, while thicker sections are unsatisfactory for visual purposes. These sections are transferred to 50 per cent ethyl alcohol until ready for use.

Many staining reactions for cellulose and lignocellulose are described in the literature, but the combination which has proved most satisfactory for this work is Haidenhain's hematoxylin and safranin. Hematoxylin is commonly supposed to stain cellulose deep purple, and similarly, safranin to stain lignocellulose red. Safranin withstands acid and alkaline treatments satisfactorily, but hematoxylin is acted upon by both; consequently sections may be stained with safranin before such treatments, but not with hematoxylin.

After staining with this combination, the following structures are purplish: the resin ducts, cells of the medullary rays, tori of the bordered pits, and in some instances a thin layer of the cell wall next the lumen. The middle lamella is deep red, while the remainder of the cell wall is of a lighter red color. There is also a marked difference in the refractive indices of these structures.

---

[1] "Wood Pulp and Its Uses," 1911, 30.

[2] *Nahr. Genussm.*, **28** (1914), 4.

[3] Missouri Botanical Garden, *Report* **1906**, 41.

[4] *Rev. Gen. Bot.*, **16** (1904), 362.

[5] Wislicenus, *Wochbl. Ppierfab*, **41** (1910), 803.

[6] Statement, Forest Products Laboratory.

[1] "Anatomy of Woody Plants," 1917, 447.

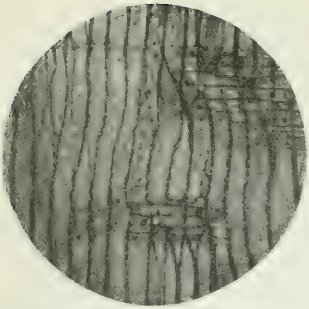


Fig. 1—Cross section of pine, 76, showing tracheids (cells or "fibers") of spring and summer growth, resin duct, and medullarly rays (heavy black lines)

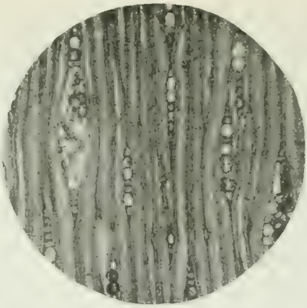


Fig. 2—Tangential section of pine, 76, showing tracheids ("fibers") and medullary rays (the latter in cross section)

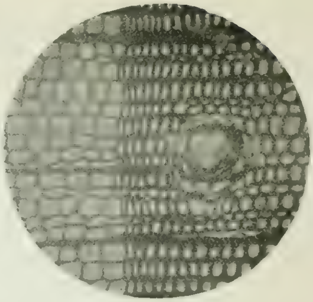


Fig. 3—Radial section of pine, 76, showing medullary rays and tracheids ("fibers") dotted with circular "bordered pits"

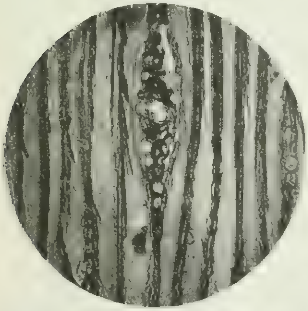


Fig. 4—Cross section of pine, 435, showing tracheids ("fibers") of spring wood; (1) "lumen" or hollow interior of cell, (2) "middle lamella" or primary cell wall, (3) later growth of cell wall

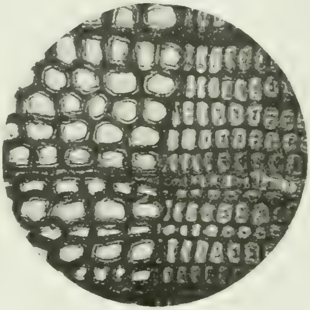


Fig. 5—Cross section of pine, 156, treated with 12N hydrochloric acid for 28 hrs. at 25O C.

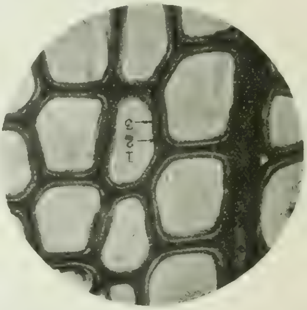


Fig. 6—Tangential section of pine, 156, threated with 12N hydrochloric acid for 28 hrs. at 25O C.

Chemical Treatment of Sections

The sections were placed in the depressions of a microscope cell slide. The cells of the slide were filled with the reagent to be studied, and a plain microscope slide was laid over the cell slide, but separated from it about 0.1 mm. by pieces of thin cover glass. The two slides were wired together and were placed in an autoclave containing a considerable quantity of the reagent. In those cases, where the reagent attacks iron considerably (*e. g.*, sodium bisulfite solution), the slides were sealed into glass tubes with the reagent. The tube containing the slide was then placed in the autoclave and was surrounded with water as the heating liquor.

This method allowed access of the reagent to the section and yet prevented destructive mechanical action. In order to follow the course of the treatment, several slides were introduced into the autoclave simultaneously. The autoclave was bolted shut and heated over a gas flame for various lengths of time at predetermined temperatures and pressures, measured respectively by a thermometer in a well and by a steam gage.

At stated intervals the autoclave was removed from the flame, cooled quickly and opened, and a slide was removed. The autoclave was again closed and heated for another interval of time.

The treated sections were washed carefully to remove adhering liquor and dirt. They were then stained and mounted in balsam for microscopic examination and measurement. Photomicrographs of these sections were made with a metallurgical microscope and camera arranged for use with transmitted light.

In some cases sections took the stains so poorly after treatment, or were so badly decomposed, that satisfactory photographs could not be obtained, although visual observations were reasonably satisfactory. Misleading optical effects due to unsatisfactory lighting sometimes occur, and must always be guarded against. In this investigation observations and measurements were made directly on the sections rather than on photomicrographs.

Measurements have been made on the cell wall, the middle lamella, and the lumen of five representative cells in both the spring and summer wood of each section. These measurements were made in a radial direction and by the use of a filar micrometer. Averages of the five readings were taken and compiled for study. While these results serve to interpret the action of various reagents, they are not sufficiently comprehensive to be taken as quantitative Measurements of the middle lamella are considerably less accurate than the others because of the comparatively slight breadth of this structure.

The effects of various reagents have been studied under different conditions of concentration, time of heating, temperature and pressure.

It must be borne in mind that the results of such experimental treatments, especially as far as the rate of action

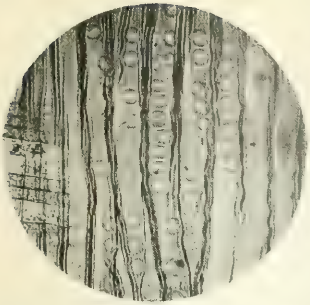


Fig. 7

Fig. 7 Radial section of pine, 156, treated with 12N hydrochloric acid for 28 hrs, at 25° C.

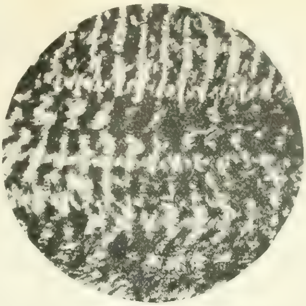


Fig. 8

Fig. 8—Cross section of pine, 156, treated with 50 per cent chromic acid for 1 min. at 25° C.

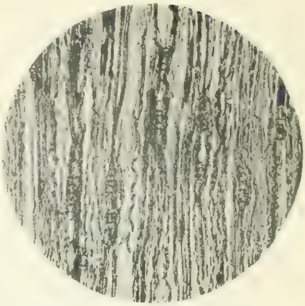


Fig. 9

Fig. 9 Tangential section of pine, 156, treated with 50 per cent chromic acid for 1 min. at 25° C.

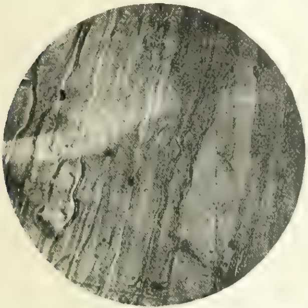


Fig. 10

Fig. 10 -Radial section of pine, 156 treated with 50 per cent chromic acid for 1 min. at 25° C.

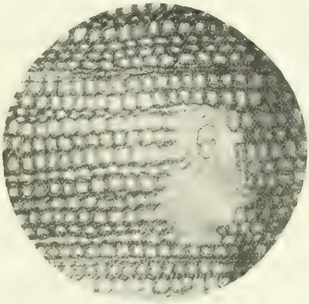


Fig. 11

Fig. 11—Cross section of pine, 90, treated with 4 per cent caustic soda soluton for 8 hrs. at 150° C .

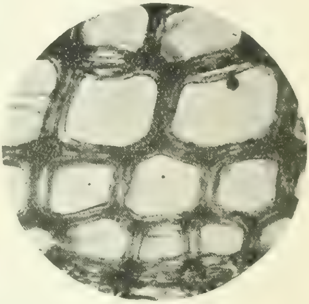


Fig. 12

Fig. 12 Cross section of pine, 465, treated with 4 per cent caustic soda solution for 8 hrs. at 150° C.

is concerned, cannot be applied directly to large-scale treatments because of the differences in such factors as penetration and quantites of material involved.

The heart wood of *Pinus Virginiana* (Jersey Pine; scrub pine) was generally used for study. The following reagents have been used in these treatments:

Distilled water
Copper ammonium reagent
10 per cent sodium chloride
72 per cent sulfuric acid
Concentrated hydrochloric acid
Phenol
Concentrated nitric acid plus potassium chlorate
Mangin's reagent (ethyl alcohol, 4 conc. HCl, 1)
50 per cent chromic acid
Lime bleach
1.0 *N* caustic soda solution
12.0 *N* caustic soda solution
10 per cent sodium bisulfite
Saturated sodium bisulfite
Saturated sulfurous acid
10 per cent sodium sulfide

Discussion of Photomicrographs

In all, about seventy sections have been made and examined. Photomicrographs have also been made of many of these sections. A detailed description of these results would obviously be out of place here; hence the discussion will be confined primarily to the following treatments as typical of the results which may be obtained by this method:

Untreated sections.
Concentrated (12 *N*) hydrochloric acid—a cellulose solvent
50 per cent chromic acid—a strong, oxidizing agent.
1.0 caustic soda—a paper-making reagent.

UNTREATED SECTIONS (Figs. 1, 2, 3, 4)—The cross section shows the dividing line between spring and summer growth, the well-marked medullary rays, and a longitudinal resin duct, surrounded by epithelial tissue. The middle lamella and bordered pits are brought out more clearly in Fig. 4.

Figs. 2 and 3 show the well-defined, overlapping tracheids (or "fibers") having the radial walls dotted with bordered pits; the numerous medullary rays and their storage contents.

CONCENTRATED HYDROCHLORIC ACID TREATMENT (Figs. 5, 6, 7)—The action of concentrated hydrochloric acid is to dissolve cellulose, probably in a more or less depolymerized and esterified form. On standing, particularly when diluted, the action on the dissolved material is largely one of hydrolsyis, with dextrose as the principal product. The lignin of coniferous wood is for the most part undissolved by this treatment, although the residue from treatments by such solvents is thought by Dore[1] to be dehydrated form of the original lignin.

In these experiments sections of wood were allowed to stand in concentrated hydrochloric acid at room temperature for 28 hrs. They were washed thoroughly and stained.

The effects of the treatment are pronounced. The cell walls are greatly swollen, particularly in the summer wood, where they have filled the lumen; the walls bulge in the middle, but are constricted at the corners. In places the cells have split away from the middle lamella, but the middle lamella itself is apparently unchanged. The medullary rays have withstood the treatment, except that some of the central cells have been removed.

FIFTY PER CENT CHROMIC ACID TREATMENT (Figs. 8, 9, 10)—Chromic acid attacks the lignin complex of lignocellulose and oxidizes it to carbon dioxide and acids of low molecular weight, such as acetic acid.[1] At the same time cellulose is attacked,[2] with the formation of oxycelluloses or decomposition products of lower molecular weight, depending upon the severity of the treatment.

---

[1] THIS JOURNAL, 11 (1919), 556.

In these experiments wood sections were treated for 1 min. in 50 per cent chromic acid at room temperature, washed thoroughly, and stained.

The action in these sections is very marked. The entire structure has evidently been attacked and partially disintegrated even in the short time involved. Cell walls are greatly swollen, the corners restricted, but the center of the wall bulging. In some places the cells have split apart and the middle lamella has been removed. The medullary rays persist, but have been distinctly attacked by the acid.

1.0 *N* CAUSTIC SODA TREATMENT (Figs. 11, 12)—The reactions of dilute caustic soda on wood, at high temperatures and pressures, are several. According to Cross and Bevan,[3] the lignin group of lignocellulose is changed into soluble products, leaving insoluble cellulose. Normal (α) cellulose is slowly attacked, but a small portion (β-cellulose) is dissolved. Pectocelluloses of the middle lamella are resolved into cellulose and soluble hydrolysis products of the noncellulose portion (pectin, pectic acid, metapectic acid), while hemicelluloses are dissolved even by cold dilute alkalies.

In these experiments wood sections were treated with 1.0 *N* caustic soda solution for various lengths of time (2, 3, 4, 6, 8, 11 hrs.). During the first 8 hrs. the temperature was maintained at 150°C. and the pressure at 65 lbs.; during the last 3 hrs. the temperature was raised to 180°C., and accordingly the pressure to 125 lbs.

The effects of the early stages of cooking on these sections will not be described as they appear more markedly in the sections treated for a longer time.

During the cooking, the cell walls swell considerably and striations appear. The resin ducts are attacked in the early stages, while the rays are acted upon gradually, and as in most other treatments retain their form after the other structures have been attacked.

The middle lamella gradually dissolves and, at the same time, splits away from the cell wall in some places. With the exception of the thickened intercellular substance at the corners of the cells (which substance persists even through the most drastic treatment), a clean channeling away of the middle lamella occurs, and consequently the tracheids are separated one from another. In the later stages of treatment the sections are badly decomposed and fall apart readily.

Discussion of Treatments

One method of studying the effects produced by these reagents is by a comparison of the measurements made on treated and untreated cells. While swelling or absence of swelling in such structures does not necessarily measure the extent of the reactions which are taking place, yet they serve to indicate the comparative effects of reagents on different portions of the structure. If, for example, a sponge were thoroughly impregnated with rubber, benzene would swell and eventually dissolve out the rubber and not affect the structure of the sponge; on the other hand, water would swell the sponge but have no effect on the rubber.

As previously pointed out, while these measurements should not be taken as absolute, the selective actions of reagents on the structures (as evidenced by changes in size, shape, and staining effects) indicate definitely that there must be a difference in composition between the structures which, for the purposes of this discussion, may be distinguished as the "middle lamella" and "cell wall." Furthermore, they show that:

1—Cellulose solvents (such as copper ammonium reagent and 72 per cent sulfuric acid) act strongly and about equally on both the middle lamella and the cell wall.

2—Strongly oxidizing solutions (such as chromic acid, bleach solutions and potassium chlorate in nitric acid) act on the cell wall but have comparatively little effect on the middle lamella.

3—The ordinary paper making reagents (such as dilute caustic soda and sodium bisulfite solutions) act strongly on the middle lamella and, relatively, have very much less effect on the cell wall.

Unfortunately it has been necessary to discontinue this investigation, at least temporarily, at a time when it gave promise of leading to more practical applications. Consequently, the evidence is too incomplete to permit of other deductions which may be allowable when additional information has been secured. For example, it is a significant fact that the ratio between the thickness of middle lamella and cell wall remains constant during treatment by cellulose solvents but varies greatly with other classes of reagents. This may argue for similarity in the amounts of cellulose in these structures, but for the presence in the cell wall of larger quantities of readily oxidizable substances than in the middle lamella.

It is to be expected that the chemicals used in paper making would react strongly on the middle lamella, but that they would react on compounds of the cell wall in such a manner as to attack the cellulose but slightly. The fact that this method brings out the evidence clearly is of great interest, because it points out the way for a systematic study of reagents which might be used in paper making.

During the progress of this work it has become increasingly evident that it would be desirable to separate the middle lamella and various portions of the cell wall, and to submit them individually to chemical analysis. This would clear up many uncertainties with regard to the structure of wood. Unfortunately, however, the individual units are so small that mechanical separation is out of the question.

The most promising method now in sight is the use of microörganisms which act only on certain parts of the cell structure. By the use of pure cultures it might be possible to treat thin sections of wood and then analyze the residual constituents. Microscopic studies should be of great assistance in such investigations, and it is not unlikely that such an investigation may open up the way for fundamentally different methods of making paper. Certainly it is becoming increasingly apparent that basic improvements in this industry can be realized only by some such a comprehensive study.

Summary

A new procedure has been developed whereby the action of chemical reagents on the microstructure of wood may be followed readily either by the microscope or by photomicrographs. This method has been used in investigating the effects of various electrolytes on pine wood. A number of typical treatments are described and discussed. The results have been studied with the microscope, photomicrographs, and by measurements with a filar micrometer.

---

[1] Cross and Bevan, "Paper Making," 1916, 42.

[2] Tromp. deHaas and Tollens, *Ann.*, 286 (1895), 296.

[3] "Paper Making," 1916, 60.

The Detection and Estimation of Coal-Tar Oils in Turpentine[1]

By V. E. Grotlisch and W. C. Smith
Leather and Paper Laboratory, Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

The detection of small quantities of coal-tar oils, such as toluene, xylene, and commercial solvent naphtha, in turpentine, and the estimation of the quantity of such adulterants present are considerably more difficult than the detection and estimation of mineral oil adulterants.

Marcusson[2] and Krieger[3] have published methods for such analyses, but these have not, in the hands of the authors, when followed most carefully, given concordant or reliable results, especially when the quantity of adulterant present was less than 10 per cent, as is frequently the case when coal-tar oils are used to adulterate turpentine fraudulently. Authentic pure gum turpentines have given results when treated according to the above methods which indicated adulteration, and samples of turpentine adulterated with as much as 2.5 and 5 per cent of solvent naphtha gave results quite similar to those obtained on pure turpentine. A brief outline of the methods referred to above may not be out of place.

Marcusson adds 10 cc. of the turpentine, drop by drop, to 30 cc. of fuming nitric acid which has previously been cooled to −10° C. by placing the flask in a freezing mixture to prevent explosion or ignition of the mixture, as the reaction is extremely violent. After standing at room temperature for about 15 min., 75 cc. of ordinary concentrated nitric acid are added, and the mixture is poured into 150 cc. of water in a flask having a narrow, graduated neck and allowed to stand on the steam bath for 15 min. The insoluble nitration product, which settles to the bottom, is then floated into the neck of the flask by adding concentrated sulfuric acid to increase the density of the liquid. The volume of the nitration product, multiplied by an empirical factor, represents the quantity of coal-tar oil present in the turpentine. Pure turpentine, according to the author, yields nitration products which go into solution in the water almost completely when heated on the steam bath, leaving only a negligibly small quantity of light resinous residue, which cannot be confounded with the heavy oily liquid nitration product obtained from the coal-tar oils.

These results are at variance with our observations. We have repeatedly obtained a considerable quantity of a viscous, gummy nitration residue from pure gum turpentine, which was insoluble in hot water, and the residues obtained in the case of authentic turpentine adulterated with commercial solvent naphtha to the extent of 3, 5, and 10 per cent, respectively, were all of very nearly the same volume as that obtained from pure turpentine, the only difference being a diminution of viscosity as the percentage of adulterant present increased. The 10 per cent residue was not free-flowing, and could not be called liquid.

Krieger shakes 20 cc. of the turpentine with 100 cc. of diluted sulfuric acid (4: 1, sp. gr. 1.76) in a flask, dilutes with 200 cc. sulfuric acid (4 : 1, sp. gr. 1.76) in a flask, dilutes with 200 cc. of water, and distils with steam. This is repeated, and the oily portion of the final distillate, which is supposed to represent total aromatic and paraffin hydrocarbons, is treated with 10 to 15 cc. of fuming sulfuric acid containing 8 per cent free SO_3, to sulfonate the benzene hydrowhich separates is considered as mineral oil, and the difference between the volume of this oil and the volume of the oily distillate obtained by the last steam distillation is calculated as benzene or coal-tar hydrocarbons.

As shown by Veitch and Donk,[4] it requires a fuming sulfuric acid, containing approximately 4 per cent free SO_3, in the proportion of 4 parts acid to 1 part turpentine, together with heating and frequent agitation at 60° to 65° C. for 10 min. to polymerize pure turpentine completely. Even then, on addition of ordinary concentrated sulfuric acid and steam distillation of the mixture, a small percentage (below 5 per cent) of a dark volatile oil with unpleasant odor, is often recovered, having a refractive index above 1.500. It is thus evident that turpentine cannot be completely polymerized by Krieger's method, and that the steam distillate will contain more or less terpene hydrocarbons. Such was found to be the case.

In order to be able to detect with certainty small percentages of coal tar oils, *i. e.,* 1 or 2 per cent, it was deemed necessary first to concentrate these oils from a large volume of sample. Fractionation was not feasible, as most solvent naphthas have initial distilling temperatures below that of turpentine, with a much wider distillation temperature range. It was found that the reaction between turpentine and dry hydrogen chloride gas offered a solution to this phase of the problem. The pinene hydrochloride crystallizes out on standing in the cold, and the non-crystallizable products have much higher boiling points, while both coal-tar oil and mineral oil are unaffected. On filtering off the crystalline pinene hydrochloride and distilling the filtrate under reduced pressure, the coal-tar oils are all concentrated in the first portions of the distillate.

By sulfonating this distillate with fuming sulfuric acid, the terpenes are polymerized into soluble, nonvolatile bodies, and the benzene hydrocarbons are converted into sulfonic acids. If the mixture is then subjected to steam distillation, a very small percentage of volatile oil, having a dark yellow color, disagreeable odor, and a refractive index at 20° C. slightly above 1.500, is recovered in the case of pure turpentine. If any mineral oil is present, it is recovered at this stage as a limpid, almost colorless oil, having the characteristic mineral oil odor and a refractive index below 1.500, usually below 1.480. Pure toluene, xylene, and solvent naphtha give no oily distillate when the sulfonation mixture is steam distilled. The coal-tar oils which are recovered, after the steam distillation no longer give any oily distillate, by the reaction first pointed out by Armstrong and Miller,[1] who showed that if the sulfonic acids of the benzene hydrocarbons, dissolved in an excess of sulfuric acid, are heated in the presence of steam to temperatures above 100° C., depending on the hydrocarbon derivative used, decomposition takes place with liberation of the free hydrocarbon. The operation is carried out by adding water, drop by drop, to the boiling acid mixture. The oils recovered in this step have always had practically the same odor and refractive index as the original coal-tar oil used as the adulterant. The recovery of any appreciable quantity of oil at this stage is an indication of the presence of coal-tar oils in the turpentine under examination.

The results obtained by the proposed method are given in Table I. It will be noted from this table that traces of oil are usually recovered in the case of pure gum turpentine. However, the small quantity of such oil recovered from pure turpentine, its odor, and the resinous gummy product obtained upon nitration, as outlined more fully below, serve to distinguish between this oil and that obtained when even small quantities of coal-tar oils are present.

It was impossible to recover the theoretical quantity of coal-tar oil which was added to the turpentine in the ex-

---

[1] Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *Chem.-Ztg.*, 36 (1912), 413, 421.

[3] *Ibid.*, 40 (1916), 972; *J. Soc. Chem. Ind.*, 35 (1916), 746a.

[4] U. S. Bureau of Chemistry, Circular 85.

[1] *J. Chem. Soc.*, 45 (1884), 150.

TABLE I RESULTS OBTAINED ON KNOWN MIXTURES OF GUM TURPENTINES AND COAL-TAR OILS

Sample No.	Nature of Sample	Adulterant Present Per cent	Adulterant Present Kind	Recovered on Steam Distillation Cc.	Recovered on Direct Distillation Cc.	Proportion of Total Coal-Tar Adulterant Recovered Per cent
1	Pure turpentine, No. 1	None		Trace	Trace	...
2	No. 1, adulterated	5	Solv. naphtha, 1	..	2.2	44
3	'' ''	4.5	'' '' 2	0.2	2.0	44.4
4	'' ''	10	'' '' 2	0.25	2.0	50
5	'' ''	2.5	'' '' 3	0.2	1.25	50
6	Pure turpentine, No. 2	None	'' ''	0.25	0.2	...
7	No. 2, adulterated	8	'' '' 3	0.3	3.2	40
8	'' ''	10	Mineral spirits	7.5	0.2	...
9	Pure turpentine, No. 3	None		0.3	0.2	...
10	No. 3, adulterated	10	C. P. xylene	0.3	5.5	55
11	'' ''	2	C. P. toluene	0.3	0.9	41
12	Pure turpentine, No. 4	None		0.3	Trace	...
13	No. 4, adulterated	2	Solv. naphtha, 1	0.3	0.8	40
14	'' ''	2	C. P. xylene	0.2	0.8	40
15	'' ''	5	Solv. naphtha, 2	4.0	2.2	44
16	'' ''	5	Mineral spirits,			
						Mean, 44.8 Factor, 2.2

periments. Hydrolysis of the sulfonic acids takes place very slowly at the temperature of initial hydrolysis, and requires a constantly rising temperature to bring about anything approaching a complete recovery of the hydrocarbons in a reasonable length of time. The reaction being a reversible one, it was found that the recovery of the hydrocarbons was better, the more rapidly the operation was carried out. However, when the temperature of the acid mixture rose to about 170° C., frothing set in, due to the resinous and carbonaceous matter formed by the action of the sulfuric acid on the terpene compounds. When the frothing became excessive, it was necessary to discontinue the distillation. The use of paraffin to prevent frothing did not prove feasible, since some of it was carried over into the distillate, introducing a corresponding error in the results. An empirical factor of 2.2, by which to multiply the quantity of oil recovered to show the true quantity present, was determined by experiment, as shown in Table I. One hundred-cc. samples were used in each experiment.

RECOMMENDED PROCEDURE

Place 100 cc. of the turpentine in a wide-mouth, 8-oz. bottle fitted with a 2-hole stopper carrying glass tubes arranged as in a gas-washing bottle. Allow to stand in a mixture of ice and salt for a short time, and then pass into the turpentine a gentle stream of hydrogen chloride gas, dried by passing through two gas-washing bottles containing concentrated sulfuric acid. A sufficient quantity of gas may be conveniently generated by gently warming 100 g. of common salt with 100 cc. of sulfuric acid made up by diluting 85 to 90 cc. of the concentrated acid. The acid is added to the salt from a dropping funnel in portions of about 20 cc. during the course of the absorption. A 3-way stopcock is placed between the generator and the first wash bottle, so that when the absorption of HCl by the turpentine is complete, the gas still being generated can be diverted readily into a bottle containing sodium hydroxide solution. The tube should not extend into the solution but just into the neck of the bottle. An ordinary 2-way stopcock is also placed between the second wash bottle and the absorption bottle, so that the former may be closed from the air while not in use. An exit tube from the absorption bottle leads into the neck of a bottle containing a little water. When the absorption of gas is complete, the excess passes on through the turpentine into this bottle, and can be seen dissolving in the water.

After the absorption is complete, disconnect the absorption bottle and allow to stand, corked, in a freezing mixture for about an hour, to obtain maximum crystallization of the pinene hydrochloride. This compound is very soluble in both mineral and coal-tar oils, so that with increasing percentages of adulteration the quantity of crystals formed becomes smaller, and scarcely any are formed at 10 per cent adulteration. Filter off the crystals on a small Hirsch funnel, with suction, and distil the filtrate under a reduced pressure equivalent to 10 in. of mercury, until crystals separate out in the condenser (which indicates complete distillation of the oils) or until 25 cc. of distillate are obtained. If the quantity of adulterant is quite large, *i.e.*, 10 per cent or more, as shown by the odor of the original sample, it will be well to collect a second 25-cc. portion of distillate and treat in the same way as the first, adding the results together. Add the distillate slowly with occasional shaking, to four times its volume of fuming sulfuric acid containing 3 to 4 per cent free SO_3, in an Erlenmeyer flask, keeping cool by holding under the water tap. Acid of 4 per cent free SO_3 content is that regularly used for testing turpentine for mineral oil, and contains 82.38 per cent total SO_3, equivalent to 100.92 per cent total H_2SO_4.[1] After the distillate has all been added to the acid, the flask is heated on the steam bath at about 70° C., for about 20 min., with frequent thorough shaking, in order to sulfonate the oils completely.

It was found that pinene hydrochloride is not readily sulfonated, and after cooling the sulfonation mixture, crystals will sometimes appear, especially when the turpentine is pure or only slightly adulterated. If the quantity is appreciable, it is advantageous to filter off these crystals on a small Hirsch funnel before proceeding. No filtering medium is needed. Dilute the sulfonation mixture cautiously with an equal volume of cold water and pass steam through it, collecting the distillate. In the case of pure turpentine, only a very small quantity (not over 0.5 cc.) of a disagreeably smelling, yellow, and rapidly darkening oil is recovered, having a refractive index at 20° C. above 1.500. If mineral oil is present, it is recovered at this point, and can be identified by its characteristic odor and refractive index, which is usually below 1.400.

When oil ceases to come over with the steam, disconnect the steam line and distil with direct heat, fitting the cork of the flask with a dropping funnel and a thermometer which extends into the liquid. After the mixture starts to boil, and when the condensate starts to show an oily portion, allow warm water to flow from the dropping funnel down the side of the flask, at a slightly slower rate than that at which it is being distilled off, to obtain a gradually increasing boiling temperature. Run the distillation at the rate of about 3 drops per sec., or about 7 to 8 cc. per min. In the case of adulteration with solvent naphtha hydrolysis starts at about 115° C. Discontinue the distillation when frothing becomes excessive, to prevent contamination of the distillate with the acid mixture. Note the quantity of oil recovered and multiply by the factor 2.2. The result will be the percentage of coal-tar oil present in the turpentine.

[1] A convenient method for preparing this acid is described in U. S. Department of Agriculture, *Bulletin* 898.

If the oil recovered is less than 0.5 cc., it may be neglected, as the quantity of adulterant, if any, is probably less than 1 per cent.

Further to identify the oil as consisting of benzene hydrocarbons, nitrate a little of it by dropping cautiously into three times its volume of fuming nitric acid, previously cooled in ice water. After warming slightly and standing aside until the action ceases, pour the mixture into cold water. A heavy, yellow to light brown, aromatic smelling oil separates out which, after washing away the excess acid, has a refractive index between 1.550 and 1.555 at 20° C. The odor is characteristic of nitrobenzene and its homologs. To carry the test still further, it may be reduced with a little zinc and hydrochloric acid, and, after neutralizing with sodium hydroxide, the amines may be recovered by steam distillation and extraction of the distillate with ether. Evaporate off the ether, acidifying with hydrochloric acid, diazotize with sodium nitrite solution, and after neutralizing with a little sodium hydroxide solution, convert into a bright scarlet azo dye by adding a few cc. of a solution of the dye intermediate known as F-acid, 2,7-β-naphtholsulfonic acid. A piece of washed wool boiled in the solution after making slightly acid with acetic acid will be dyed a bright scarlet, fast to light. Other intermediates of the general nature of F-acid may be used, if the latter is not available, but F-acid gives the brightest solution.

Wood turpentines, both steam and destructively distilled, do not give reliable results when tested by the above procedure, probably because the high temperatures to which the wood and the resinous constituents thereof are exposed in present methods of manufacture partly break down the terpenes and resins to simple ring hydrocarbons. Both toluene[1] and *m*-isopropyltoluene, or *m*-isocymene[2] have been identified in rosin spirits, the low-boiling fraction from the destructive distillation of rosin. The destructively distilled wood turpentines, as was to be expected, gave considerably higher yields of oil from the distillation of the sulfonation mixture than the steam distilled wood turpentines. The wood in the steam distillation process, being treated with superheated steam, is not subjected to such high temperatures as to decompose the rosin materially, as in the destructive distillation process. This is being studied further.

SUMMARY

A method has been devised for detecting and estimating the percentage of coal-tar oils in gum turpentine adulterated therewith. The method will also serve to detect the presence of mineral oils if any be present.

As a result of certain causes not fully understood, the recovery of coal-tar oils is, on the average, about 45 per cent of the theoretical, requiring that the quantity of oil recovered be multiplied by the factor 2.2.

In order to obtain concordant results, the strength of the sulfuric acid used to decompose the turpentine must be definite, varying between 3 and 4 per cent free SO_3.

A method for further identifying the oils obtained in the last step of the analysis has also been described.

The method is not strictly applicable to wood turpentine, because small quantities of the coal-tar oils are often found as normal constituents of this kind of turpentine. However, any considerable recovery of oil from the sulfonation mixture, *i.e.*, 4 per cent or more, even in the case of destructively distilled wood turpentine, will serve to throw suspicion on the purity of the turpentine.

A Revision of the Optical Method for Analyzing Mixtures of Sucrose and Raffinose[1]

By C. A. Browne and C. A. Gamble

The New York Sugar Trade Laboratory, Inc., 80 South St., New York, N. Y.

One of the most interesting sugars from a chemical and analytical standpoint is the trisaccharide, raffinose. This sugar, first indicated by Johnston[2] in *Eucalyptus manna* in 1843, was afterwards investigated in 1856 by Berthelot,[3] who gave it the name melitose. In 1876 Loiseau[4] discovered in the impure molasses of a beet-sugar refinery an unknown high polarizing sugar to which he gave, from the place of its occurrence, the name raffinose. In 1884 Böhm[5] announced the discovery in cottonseeds of a new sugar to which he gave the name gossypose. Tollens[6] in 1886 proved melitose and gossypose to be identical with Loiseau's raffinose. This identification was important, for it established the wide occurrence of raffinose in the vegetable kingdom. The sugar has been found also in young wheat sprouts, in barley, and in other plant substances; careful investigation would no doubt show it to be widely distributed.

Raffinose is almost always associated in nature with sucrose, and the importance of devising a method for estimating these two sugars when they occur together was quickly recognized, especially in the analysis of beet sugars, where the presence of only a slight amount of raffinose may cause the polarization of a sugar to exceed 100.

Owing to the fact that raffinose is hydrolyzed by the ordinary methods of acid inversion and undergoes a decrease in polarizing power, the customary Clerget method for determining sucrose was found to be no longer applicable to sucrose-raffinose mixtures. Creydt,[3] however, found that when a separate formula for estimating raffinose is united with the familiar Clerget formula, a combined equation can be derived which permits the estimation of the two sugars with a fair degree of accuracy.

With the later substitution of the Herzfeld modification in place of the old Clerget process of inversion, the Creydt formulas for estimating sucrose and raffinose were revised in order to conform to the new conditions. These revised formulas, as given by Herzfeld,[4] are

$$S = \frac{0.5124\ P - P'}{0.839} \text{ and } R = \frac{0.3266\ P + P'}{1.554}$$

in which S and R are respectively the percentages of sucrose and raffinose, and P and P′, respectively, the direct and invert polarizations at 20° C.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *J. prakt. Chem.*, [1] **29** (1843), 485.

[3] *Ann. Chim.*, [3] **46** (1856), 66.

[4] *Compt. rend.*, **82** (1876), 1058.

[5] *J. prakt. Chem.*, [2] **30** (1884), 37.

[6] *Ann.*, **232** (1886), 169.

[1] Pelletier and Walter, *Ann. chim. phys.*, [2] 67 ([illegible]), 278; Kelbe, *Ann.*, 210 (1881), 14.

[2] Kelbe, *Loc. cit.*

[3] *Z. Ver. deut. Zuckerind.*, **37** (1887), 153.

[4] *Z. Ver. deut. Zuckerind.*, **40** (1890), 194.

PURPOSE OF INVESTIGATION

Previous to 1910 considerable doubt began to be expressed among chemists as to the accuracy of the Herzfeld divisor 142.66 in the Clerget formula, and in 1912 a committee was appointed by the International Commission for Uniform Methods of Sugar Analysis to determine the exact value of this factor. The outbreak of the war prevented the International Commission from meeting again, and for general purposes the Herzfeld divisor 142.66 still continues in common use. Langguth-Steuerwald[1] in 1913 determined the Clerget divisor for Herzfeld's process of inversion to be 143.05. Schrefeld,[2] in a posthumous paper published in September 1920, of a research conducted in Herzfeld's laboratory in 1910, found the Clerget divisor to be exactly 143, and stated that the erroneous value 142.66 was probably due to its having been established for a preparation of sucrose that contained raffinose as an impurity. The writers of the present paper also find a value of 143, which corresponds to a Clerget divisor of 133 with a negative constituent of —33 at 20°C., when following the process of inversion recommended by Schrefeld. This correction in the inversion constant for pure sucrose obviously necessitates another revision of the modified Creydt formulas for analyzing mixtures of raffinose and sucrose, and this was one of the purposes which the writers had in mind when beginning the present investigation.

A second purpose in connection with this research was the redetermination of the inversion constant of pure raffinose. For this purpose two preparations of chemically pure raffinose were used, one of foreign and the other of domestic manufacture. The foreign product, manufactured by Kahlbaum, consisted of fine white crystals of raffinose hydrate, which on drying in a vacuum, first at 70°C. and afterwards at 100°C., lost 15.18 per cent water; the theoretical loss for $C_{18}H_{32}O_{16}.5H_2O$ is 15.16 per cent water. The crystals of the hydrate dissolved in water to a perfectly colorless solution and gave a specific rotation upon a quartz wedge saccharimeter corresponding to $[\alpha]^{20°}_{D} = +104.42$. The average value for the specific rotation of raffinose hydrate according to Landolt, Tollens, Lippmann, and other authorities is $[\alpha]^{20°}_{D} = +104.5$.

The raffinose of domestic manufacture was a preparation of the anhydrous sugar, which, either from imperfect dehydration or from reabsorption of atmospheric moisture, contained considerable raffinose hydrate. The product gave a specific rotation upon the saccharimeter corresponding to $[\alpha]^{20°}_{D} = +119.8$, which would correspond to a mixture of about 82 per cent anhydride and 18 per cent hydrate. It lost upon drying in vacuo over sulfuric acid, first at 60°C. and then at 95°C., 2.71 per cent moisture. The specific rotation when corrected for this amount of moisture, is $[\alpha]^{20°}_{D} = +123.14$, which agrees very closely with the generally accepted value of $+ 123.2$.

DETERMINATION OF INVERSION COEFFICIENT OF RAFFINOSE

For determining the inversion coefficient of raffinose, the process recommended by Schrefeld for the inversion of sucrose was followed. Several solutions of different concentration were polarized at exactly 20°C., 50 cc. of these solutions were measured into 100-cc. flasks, water was added to bring the total amount of water in each flask to 75 cc., 5 cc. of HCl (sp. gr. 1.19) were added, and the flasks were immersed in a large water bath kept at exactly 70°C. A thermometer was placed in each flask, which was gently rotated. In about 3 min. the temperature of the solutions in the flasks reached 67°C., from which point the heating was continued exactly 5 min. longer. The temperature at the end of the heating was 69.5°C. The flasks were quickly cooled, and after rinsing off the thermometers the solutions were made up to 100 cc. at 20°C., mixed, and polarized at this temperature in a quartz wedge saccharimeter, using a 400-mm. tube. The results obtained with six solutions of raffinose are recorded in Table I. The saccharimeter readings were taken by four observers on two different instruments, and the average values recorded.

TABLE I RATIO OF DIRECT TO INVERT POLARIZATION OF RAFFINOSE SOLUTIONS

Raffinose Preparation	Direct Polarization (P) 200-mm. Tube, 20° C.	Invert Polarization (P′) 400-mm. Tube, 20° C.	Ratio $\frac{P'}{P}$
Kahlbaum	+99.69	+51.21	0.5137
Kahlbaum	+99.63	+51.22	0.5141
Domestic	+57.20	+29.46	0.5150
Kahlbaum	+26.95	+13.86	0.5143
Domestic	+12.80	+ 6.59	0.5148
Kahlbaum	+ 7.44	+ 3.82	0.5134
	Average		0.5142

In the present paper the rounded three-decimal value 0.514 is taken as the basis of calculation. This is a little higher than the value used in the Herzfeld formula, which is 0.5124. The values reported by other observers for different methods of inversion are 0.5070 by Creydt,[1] 0.5182 by Dammüller,[2] 0.5188 by Lippmann,[3] and 0.5094 by Beythien and Tollens.[4] Variations in the concentration of raffinose seem to have but little influence upon the ratio.

EVALUATION OF FORMULAS FOR ESTIMATION OF SUCROSE AND RAFFINOSE

The evaluation of the formulas for estimating sucrose and raffinose, on the basis of the invert factor —0.33 for sucrose and + 0.514 for raffinose, is made as follows:

The generally accepted ratio of the specific rotation of sucrose to that of raffinose anhydride is $\frac{+123.2}{+66.5} = 1.852$.

If the sucrose normal weight of a product be taken, the direct polarization (P) of S per cent sucrose and R per cent raffinose, upon a saccharimeter, would be represented by the equation

$$P = S + 1.852\,R \qquad (1)$$

$$\text{whence } R = \frac{P - S}{1.852} \qquad (2)$$

$$\text{and } S = P - 1.852\,R \qquad (3)$$

The polarization of S per cent sucrose at 20°C. after inversion (disregarding the influence of concentration) would be — 0.33 S, and the polarization of R per cent raffinose at 20°C. after inversion would be 1.852R × 0.514. The total invert polarization (P′) at 20°C. of the mixture of sugars is then

$$P' = -0.33\,S + (1.852\,R \times 0.514) \qquad (4)$$

Substituting for R in Equation 4 its value from Equation 2 we obtain

$$P' = -0.33\,S + 0.514\,(P - S) \qquad (5)$$

$$\text{whence } S = \frac{0.514\,P - P'}{0.844} \text{ at } 20° \text{ C.} \qquad (6)$$

Substituting for S in Equation 4 its value from Equation 3 we obtain

$$P' = -0.33\,(P - 1.852\,R) + (1.852\,R \times 0.514) \qquad (7)$$

$$\text{whence } R = \frac{0.33\,P + P'}{1.563} \text{ at } 20° \text{ C.} \qquad (8)$$

Formulas 6 and 8 are valid only when the solutions are made up and polarized at exactly 20°C., and a third pur-

---

[1] *Arch. Suikerind.*, 21 (1913), 1383.

[2] *Z. Ver. deut. Zuckerind.*, **70** (1920), 402.

---

[1] *Ber.*, **19** (1886), 3115.

[2] *Z. Ver. deut. Zuckerind.*, **38** (1888), 748.

[3] *Z. Ver. deut. Zuckerind.*, **38** (1888), 1232.

[4] *Z. Ver. deut. Zuckerind.*, **39** (1889), 917.

pose of the present investigation was the evaluation of a general formula that would be applicable at all temperatures.

Evaluation of General Formula Applicable at All Temperatures

TEMPERATURE COEFFICIENT FOR SUCROSE—The influences of changes in temperature upon the direct and invert polarization of sucrose upon quartz-wedge saccharimeters have been very thoroughly investigated, and are expressed by the general equation

$$P = S\,[1 - 0.0003\,(T - 20)] = S\,(1.006 - 0.0003\,T)$$

for the direct polarization (P) and

$$P' = S\,[-0.33 + 0.005\,(t - 20)] = S\,(-0.43 + 0.005t)$$

for the invert polarization (P′), S being the percentage of sucrose, T the temperature of the direct polarization, and t the temperature of the invert polarization.

TEMPERATURE COEFFICIENT FOR RAFFINOSE—There is very little information in the chemical literature as to the influence of temperature changes upon the direct polarization of raffinose. Creydt[1] states that the rotation of raffinose undergoes a slight decrease with increase in temperature. Other authorities state the influence of temperature changes to be imperceptible or negligible. The writers, from measurements of the polarization of raffinose solutions made up and polarized at 10° C. and of similar solutions made up and polarized at 32° C., observed a decrease in polarization with increase in temperature, this decrease amounting to 0.00034 for each degree of the saccharimeter scale for 1° C. increase in temperature. This value differs by only 0.00004 from that obtained for sucrose. The temperature correction for sucrose may, therefore, be applied to the direct polarization of raffinose on quartz-wedge saccharimeters without sensible error. Equation 1 for the direct polarization at temperature T of a sucrose normal weight of product containing S per cent sucrose and R per cent raffinose would then be

$$P = S\,(1.006 - 0.0003\,T) + 1.852\,R\,(1.006 - 0.0003\,T) \qquad (9)$$

Several formulas have been worked out for correcting the invert polarization of raffinose for changes in temperature. Herles[2] found a solution of raffinose, which polarized +100 at 20° C. upon the saccharimeter before inversion, to read, after inversion by Herzfeld's method, +51.24 when the inverted solution was made up and polarized at 20° C., and to read +47.24 when the inverted solution was made up and polarized at 0° C., which corresponds to a loss of 0.2 in polarization for 1° C. decrease in temperature.

The writers found a solution of raffinose, which polarized +100 at 20° C. before inversion, to read, after inversion by Schrefeld's modification, +53.54 when the inverted solution was made up and polarized at 32° C., and to read +49.61 when the inverted solution was made up and polarized at 10° C., which corresponds to a loss of 0.18 in polarization for 1° C. decrease in temperature. The temperature correction for the invert polarization of a solution of raffinose, polarizing +100 at 20° C. before inversion upon a quartz-wedge saccharimeter, is therefore $+51.4 + 0.18\ (t - 20) = +47.8 + 0.18t$, which, calculated to a solution of raffinose having a direct polarization of +1, would be $+0.478 + 0.0018t$. The temperature correction for the invert polarization of sucrose, employing Schrefeld's modification of Herzfeld's process, is $-33.0 + 0.5(t - 20) = -43.0 + 0.5t$, which, divided by 100, equals $-0.43 + 0.005t$ for a direct polarization of +1 at 20° C. Equation 4 for the invert polarization at temperature t of a sucrose normal weight of product containing S per cent sucrose and R per cent raffinose would then be

$$P' = S\,(-0.43 + 0.005t) + 1.852\,R\,(+0.478 + 0.0018t) \qquad (10)$$

Substituting in (10) the value of R from Equation 9 we obtain

$$S = \frac{P(0.478 \times 0.0018t) - P'(1.006 - 0.0003\,T)}{(0.908 - 0.0032t)\,(1.006 - 0.0003\,T)} \qquad (11)$$

Substituting in (10) the value of S from Equation 9 we obtain

$$R = \frac{P(0.43 - 0.005t) + P'(1.006 - 0.0003\,T)}{(1.681 - 0.0059t)\,(1.006 - 0.0003\,T)} \qquad (12)$$

When T and t are each 20° C., Equations 11 and 12 become necessarily the same as (6) and (8).

Applications of the preceding formulas to the analysis of several mixtures containing known amounts of sucrose and raffinose are given in Table II.

TABLE II—ANALYSIS OF KNOWN MIXTURES OF SUCROSE AND RAFFINOSE

Taken		Observed				Calculated	
Sucrose Per Cent	Raffinose Per Cent	P	T °C.	P′	t °C	Sucrose Per Cent	Raffinose Per Cent
96.06	3.25	+102.00	20	28.68	20	96.09	3.19
92.22	6.51	+104.30	20	24.30	20	92.31	6.48
76.85	7.47	+ 90.72	20	18.25	20	76.87	7.48
76.85	7.47	+ 90.50	30	-14.26	30	76.90	7.46

In making the analyses of Table II, only the most carefully graduated flasks and observation tubes were employed, and the measured volumes of solution used for inversion were checked by weighing. The work was performed in an insulated constant temperature room, and the average readings of two observers were taken as the recorded values of P and P′.

With mixtures containing low percentages of sucrose, the negative constituent —33 of the Clerget divisor requires a slight modification for changes in concentration, and this necessitates a small correction of the revised formulas given in this paper. This correction is most easily applied by the method of approximation. For pure sucrose the negative constituent of the Clerget divisor for the Schrefeld-Herzfeld formula varies according to the equation

$$N = -(32.1 \times 0.07g)$$

in which g is the grams of sucrose in the half normal weight of substance taken for inversion. After determining the approximate percentage of sucrose by means of Formulas 6 or 11, the value of g is found, and from this the calculated value of the negative constituent (N) is determined. The value of 0.01 N is then substituted for —0.33 in Formula 5, and the corrected formulas for S and R are evaluated as previously described.

Thus, for a beet molasses containing 50 per cent sucrose, $g = 6.5$, whence $N = -(32.1 + 0.07 \times 6.5) = -32.6$ and $0.01\ N = -0.326$. Formula 5 as thus corrected would give

$$S = \frac{0.514\ P - P'}{0.84} \text{ and } R = \frac{0.326\ P \times P'}{1.556} \qquad (13)$$

In mixtures containing low percentages of sucrose and high percentages of raffinose the concentration of the inverted sucrose solution is affected so that this method of correction is no longer strictly valid. The products met with in commercial analysis contain, however, for the most part only small percentages of raffinose, so that the question of high raffinose mixtures has nit a wide practical significance. In mixtures of sucrose with other sugars the negative constituent of the Clerget divisor varies with the total carbohydrate concentration and not with the concentraion of sucrose alone.

The Influence of Impurities Upon the Estimation of Sucrose and Raffinose by the Optical Method

While the results of Table II indicate that the optical method may give concordant results in the analysis of pure mixtures of sucrose and raffinose, no conclusion can be drawn as to the relative accuracy of this method in the analysis of mixtures of these sugars with the salts, nitrogenous substances, and other impurities that are found in natural and commercial products. The question of impurities and of their influence upon the accuracy of the method introduces so many complications that only a few simple instances can be considered in the present paper. The following cases are taken: (1) Influence of optically inactive salts, (2) influence of optically active amino compounds, and (3) influence of clarifying agents. In this connection the analysis of such a product as sugar-beet molasses is chiefly considered.

---

[1] *Z. Zuckerind. Bohmen*, **13** (   ), 559; **15** (   ), 528.

[2] *Z. Ver. deut. Zuckerind.*, **37** (1887), 153.

INFLUENCE OF OPTICALLY INACTIVE SALTS—Ordinary beet molasses contains about 8 per cent of various organic and inorganic salts of potassium, about 1 per cent of the chloride and other salts of sodium, and a small remainder consisting principally of calcium salts. Potassium and sodium salts are the principal disturbing factors. Organic and inorganic salts of the alkalies, according to the results of different investigators, produce generally a pronounced decrease in the polarization of sucrose. The results in the case of raffinose are less marked, there being either no change or else a slight increase in polarization. Washburn[1] obtained an increase in the polarization of raffinose on the addition of potassium and sodium chlorides. The writers selected potassium oxalate as a convenient salt for experiments, and, with the proportion of 3 g. $K_2C_2O_4.H_2O$ in 100 cc., obtained the following results for the direct and invert polarization of sucrose and raffinose.

	P		P′	
	Without Oxalate	With Oxalate	Without Oxalate	With Oxalate
Sucrose	+50.00	+49.75	—16.40	—16.50
Raffinose	+17.13	+17.20	+ 8.85	+ 8.93

A decrease of 0.25 is observed in the direct polarization of sucrose, an increase of 0.07 in the direct polarization of raffinose, an increase of 0.10 in the invert polarization of sucrose, and an increase of + 0.08 in the invert polarization of raffinose. The effect of these influences in the analysis of a mixture of sucrose and raffinose is partly compensating. A normal weight of a mixture containing 50 per cent sucrose, 9.25 per cent raffinose, and 11.54 per cent $K_2C_2O_4.H_2O$, dissolved to 100 cc., gave a value of + 66.95 for P and —7.57 for P′. The percentages, as calculated by Formula 13, would then be 49.98 per cent sucrose and 9.16 per cent raffinose. We may, therefore, conclude that the presence of optically inactive salts of potassium and sodium in such amounts as occur in sugar-beet molasses will not produce errors exceeding 0.1 or 0.2 per cent

INFLUENCE OF OPTICALLY ACTIVE AMINO COMPOUNDS—Among the optically active amino compounds which have been detected in sugar-beet products are asparagine and glutamine, and the corresponding derivatives of these, aspartic and glutaminic acids. The presence of any foreign, optically active substance introduces an error in the estimation of sucrose and raffinose by the optical method. Thus a foreign substance affecting the determination of P and P′ to the extent of + 0.1 would make the calculated percentage of sucrose 0.06 too low and the calculated percentage of raffinose 0.09 too high. When, however, the foreign, optically active substance has a different polarization in neutral and acid solution, as is the case with the optically active amino compounds, these errors of method are greatly increased. The following approximate specific rotations are given for several amino substances in water and in the presence of hydrochloric acid:

	WATER	IN PRESENCE OF HCl
Asparagine	— 6	+34
Aspartic acid	+ 4	+34
Glutamine	0	+30
Glutaminic acid	+10	+30

The marked increase in dextrorotation of these substances in the acid inverted solution causes a pronounced diminution in the calculated percentage of sucrose and a pronounced increase in the calculated percentage of raffinose. Thus, a mixture of amino substances having an influence of —0.1 upon P and of +0.5 upon P′ would make the calculated percentage of sucrose 0.66 too low and the calculated percentage of raffinose 0.30 too high. In other words, application of the method to a mixture of sucrose and asparagine would indicate the presence of raffinose when this sugar was entirely absent, as may be seen from the following example. A mixture containing 50 per cent sucrose and 3.85 per cent asparagine gave a value of + 49.65 for P and of — 14.8 for P′. Application of Formulas 13 indicate 48.00 per cent sucrose and 0.86 per cent raffinose.

Ehrlich,[1] Andrlik and Stanek,[2] Smolenski,[3] and other chemists have called attention to the errors which may result from the presence of optically active amino compounds in the analysis of beet products, and for a more detailed account of such errors the original papers of these investigators should be consulted.

INFLUENCE OF CLARIFYING AGENTS—In this connection the influence of basic acetate of lead as a clarifying agent is alone considered. The errors due to the use of this reagent are of two kinds, first the error due to the volume of the lead precipitate, and second, the error due to the effect of any excess of lead subacetate upon the polarization of optically active substances.

The error due to the volume of the lead precipitate produces an increase in the percentages of sucrose and raffinose as calculated from the direct and invert polarizations. For a normal weight of 26 g. of beet molasses the volume of lead precipitate may equal 1 cc., which, for a product containing 50 per cent sucrose and 5 per cent raffinose, would produce an increase of 0.50 in the percentage of sucrose and of 0.05 in that of raffinose

The action of dissolved lead subacetate upon the polarization of optically active substances is variable. In the case of sucrose, the results of Bates and Blake[4] show a slight decrease for amounts of lead solution not exceeding 6 cc. For volumes of lead solution exceeding 6 cc. a gradual increase in polarization was noted. In the case of raffinose small amounts of lead subacetate produce no change in polarization; larger amounts, according to Weisberg[5] and to Svoboda,[6] cause a decrease. An experiment of the writers showed that a solution of raffinose made up to 100 cc. with water and 10 cc. of lead subacetate solution of 1.26 sp.gr. underwent a decrease in polarization from +34.25 (the reading for a pure aqueous solution) to +32.90.

Lead subacetate causes the polarizations of asparagine and aspartic acid to deviate strongly to the right, and those of glutamine and glutaminic acid to deviate slightly to the left. Experiments by Smolenski,[7] upon the mixture of amino substances in the waste saccharate liquor of a beet sugar factory, showed that 5 cc. of lead subacetate in

---

[1] *J. Am. Chem. Soc.*, **31** (1909), 338.

[1] *Z. Ver. deut. Zuckerind.*, **53** (1903), 809.

[2] *Z. Zuckerind. Bohmen*, **31** (1906-7), 417.

[3] *Z. Ver. deut. Zuckerind.*, **60** (1910), 1215: **62** (1912), 791.

[4] U. S. Bureau of Standards *Bulletin* **3**, 105.

[5] *Bull. assoc. chim. sucr. dist.*, **9** (1891), 498.

[6] *Z. Ver. deut. Zuckerind.*, **46** (1896), 107.

[7] *Z. Ver. deut. Zuckerind.*, **62** (1912), 804.

100 cc. of solution caused the direct polarization to decrease from + 1.50 to + 1.25 and that 5 cc. of hydrochloric acid in 100 cc. of solution caused the invert polarization to increase from + 1.50 to + 2.70. The effect of lead subacetate, according to the nature of the amino compounds present, might therefore cause an increase as well as a diminution in the errors which these foreign optically active substances produce. The sum of all the influences of lead subacetate upon the errors of the optical method for analyzing sucrose-raffinose mixtures would seem, however, generally to be compensating, the errors being usually less with than without its use. This is shown by Table III, which gives a general summary of the results obtained in the analysis of mixtures of sucrose and raffinose with potassium oxalate and asparagine, both in presence and in absence of lead subacetate.

TABLE III SHOWING INFLUENCE OF IMPURITIES UPON THE ESTIMATION OF SUCROSE AND RAFFINOSE

	TAKEN					OBSERVED		CALCULATED	
No.	Sucrose Per cent	Raffinose Per cent	Potassium Oxalate Per cent	Asparagine Per cent	Lead Subacetate	P	P′	Sucrose	Raffinose
1	50.00	9.25	...	...	.	+67.13	7.55	50.06	9.21
2	50.00	9.25	11.54	.	.	+66.95	−7.57	49.98	9.16
3	50.00	9.25	..	3.85	.	+66.78	−5.85	47.83	10.23
4	50.00	9.25	11.54	3.85	.	+66.80	−5.90	47.89	10.20
5	50.00	9.25	11.54	3.85	10 cc.	+67.18	6.20	48.49	10.09

There are two possibilities for improving the accuracy of the inversion methods for estimating sucrose and raffinose—one by the use of an inverting agent, such as invertase, which avoids the disturbances produced by free acid in polarization of the amino substances, and the other by use of precipitating agents which remove the acid after inversion from solution.[1] Both of these possibilities are being examined by the writers, who hope to report upon them at a later time.

SUMMARY

The change in the Herzfeld divisor of the Clerget formula for estimating sucrose from 142.66 to 143 has necessitated a revision of the Creydt formula for analyzing mixtures of sucrose and raffinose. In the course of this revision, the inversion constant of raffinose and the temperature coefficient for the polarization of raffinose before and after inversion have been redetermined.

The relative accuracy of this revised formula is illustrated in the case of known mixtures of sucrose and raffinose and in the case of known mixtures of these sugars with potassium oxalate and asparagine when lead subacetate is used as a clarifying agent. Possibilities of improving the optical method for analyzing mixtures of sucrose and raffinose are also indicated.

---

[1] R. F. Jackson and C. L. Gillis (Bureau of Standards *Scientific Paper* 375. 177) suggest a modification of the Creydt method, which consists in neutralizing the inverted solution with ammonium hydroxide and adding the equivalent amount of ammonium chloride to the solution for the direct polarization, in order to secure equality of conditions before and after inversion. This suggestion, which has not been worked out in detail, deserves consideration.

Shortening: Its Definition and Measurement[1, 2]

By Clark E. Davis

NATIONAL BISCUIT CO., 409 W. 15TH ST., NEW YORK, N. Y.

The term "shortening" has never been satisfactorily defined. Still less satisfactory have been the attempts to measure it.

The term is used throughout this paper as related to crackers, biscuits, or cakes. The average baker tests the shortness of a cracker in two ways: (1) by its resistance to breaking, and (2) by its resistance to crushing. This is natural in view of the fact that in eating a cracker the shortness is first apparent when it is broken, either by the aid of the hands or by the teeth. It is even more apparent in the chewing operation, which is really one of grinding or crushing. Consequently if some method could be devised which would measure either the breaking strength or the crushing strength, or both, it might lead to a definition of the term "shortening."

With this idea in mind, a machine has been devised which will measure either the breaking strength or the crushing strength with a high degree of accuracy. This machine is similar to the forms of cement testing machines commonly in use. These machines, however, are designed for measuring heavy loads, and their sensitiveness need not be of the highest order of accuracy. The force required to break or crush any food product, such as those with which we are working, is necessarily very small. This requires that the measuring machine be extremely sensitive in order to obtain great accuracy. In a cement briquet a force of six, seven, or eight hundred pounds is required, while for a cracker a force of two, three, or four pounds is necessary.

APPARATUS

The machine[3] described in this paper has been devised for measuring breaking strength and crushing strength. It will be hereafter referred to as a "shortometer."

In the drawing, Fig. 1 represents a side elevation of one form of the testing device. Fig. 2 is a horizontal section taken upon line 2—2 of Fig. 1, size of base 4.5 in. × 6 in. Fig. 3 is an end elevation of the lower portion of the ap-

Fig. 1.

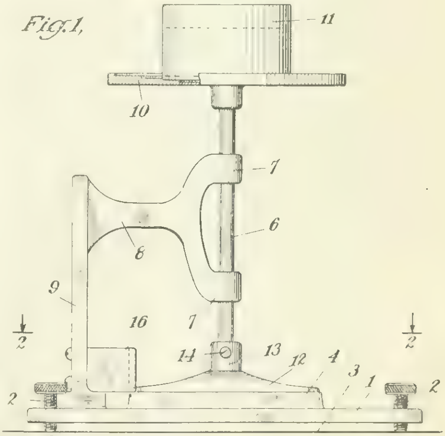
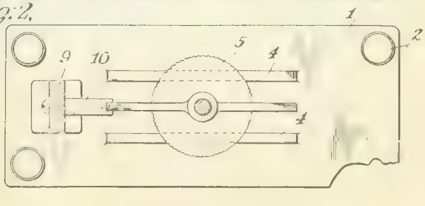


Fig. 2.



---

[1] Received May, 5, 1921.

[2] Published as Contribution No. 2 from the Research Laboratory of The National Biscuit Company.

[3] Patent applied for.

Fig. 3

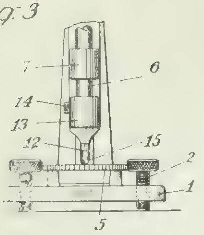
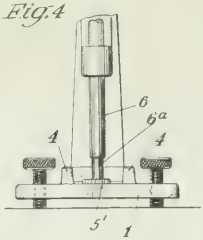


Fig. 4



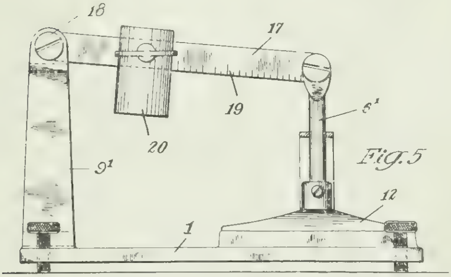


Fig. 5

paratus shown in Fig. 1, engaged in breaking a test cake. Fig. 4 is similar to Fig. 3, showing the test of a sample cake for its resistance to crushing. Fig. 5 is a side elevation of a modified form of testing apparatus.

In the apparatus shown in Figs. 1 to 4, inclusive, a table, 1, is supported on 3 by means of adjustable screws, 2.

A pair of parallel rails, 4, extend upward from table 1 to support the cake, 5, when tested for breaking strength. A vertical hardened steel rod, 6, 5 in. long is mounted in vertical hardened steel bearings, 7, formed on a lateral extension, 8, of a vertical standard, 9, which is mounted on table 1. Spindle 6 carries a horizontal support, 10, at its upper end, on which a shot container, 11, is stationed. The striking member, 12, elongated, in socket 13 with setscrew 14 is detachable from spindle 6 and is preferably rounded and comparatively narrow (See 15, Fig. 3). 16 is a guideway for the striking member.

When a cake is to be broken it is positioned across the rails 4, and member 12 is placed thereon, while shot is run into container 11 until the point of rupture occurs. The container and contents are then weighed.

A modified form of apparatus is shown in Fig. 5 in which the spindle, 6′, is pivotally connected to an arm, 17, which is pivoted at 18 to the standard 9′. Arm 17 carries a graduated scale as indicated at 19 and a sliding weight, 20.

When it is desired to test the crushing strength a portion of the cake, as indicated at 5′ in Fig. 4, may be placed on table 1 between the rails, 4, so that the cake rests firmly on the table. Striking member 12 is removed from spindle 6 by unscrewing set-screw 14. The lower portion, 6_a, of spindle 6 has a horizontal bottom surface of comparatively small diameter. Shot is allowed to flow into the container 11 until the spindle crushes or pulverizes that portion of the cake against which it rests. The container with contents is then weighed.

EXPERIMENTAL

In searching for a type of goods upon which the experiments were to be made it was decided to use a variety of sugar cooky, because the amount of shortening used is a fair average and the cake is easily made.

The following formula was used:

196 lbs.	flour, medium winter
35 lbs.	shortening
80 lbs.	sugar
43.8 lbs.	water
0.5 lbs.	salt
0.5 lbs.	ammonium bicarbonate
0.3 lbs.	monocalcium acid phosphate
1.5 lbs.	sodium bicarbonate

All the experimental batches were 1 per cent of the original formula. This produced 3.5 lbs. of dough.

In order to arrive at some definite method of procedure several hundred batches of cakes, made with the various shortening agents, were tested for their shortness.

Standardized conditions must be established. In the manufacture of a cake there are many variables, *e. g.*, exact amount of material used, method of mixing,[1] temperature of dough while mixing, time of mixing, the pressure exerted by the brake, temperature of baking oven, conditioning of the cake after baking, etc.

In the experimental work these conditions have all been so standardized that each cake gets the same treatment as every other one. The materials are all accurately weighed, the mixing is done by machine, the doughs are all made as near the same temperature as possible, which is 80° F., the time of mixing is 7 min., the brake treatment gives all green cakes the same thickness, three-thirty-seconds of an inch, and the cakes are always cut of the same diameter, two and five-sixteenths inches.

The temperature of baking is 465° F., and in the reel oven used this was controlled to ± 2.5° by means of an electric control of the gas supply. The oven temperature is undoubtedly not uniform throughout, but this irregularity is obviated by the use of the reel oven which takes the cake through the relatively hot and cold zones, thereby giving all uniform treatment. Each batch is baked for the same length of time (8.25 min.), determined by the number of revolutions (6).

The product is cooled in the absence of drafts to prevent checking. It is then conditioned for at least 48 hrs. in a closed cabinet where the temperature and humidity remain practically constant. At the end of this time the cake is broken in the shortometer. All cakes are of approximately the same diameter and are always placed in the same relative position.

Several hundred cakes were used in testing some shortenings, while in some cases as many as three thousand were used in the standardization of this apparatus.

A few results are given, showing the method of recording and the breaking strength of each individual cake in various batches:

TABLE I

Kind of fat	No. 1 Lard	No. 2 Lard	No. 3 Lard	No. 4 Lard
Date of baking	July 10	July 17	July 24	July 26
Date of test	July 12	July 19	July 26	July 28
Temp. of dough, °F.	79	81	80	81
Temp. of room, °F.	77	80	84	91
Temp. of oven, °F.	465	465	465	465
Humidity, per cent	63	79	66	62
	Breaking strength, Lbs.			
	2.63	2.63	3.06	2.63
	2.75	2.88	2.69	3.38
	2.75	3.06	2.94	2.94
	3.13	2.88	2.94	2.75
	2.88	2.94	2.94	2.63
	3.06	2.94	2.56	2.94
	2.88	2.63	3.00	2.94
	2.88	3.25	2.88	2.69
	2.69	2.88	3.06	2.88
	2.94	3.50	2.81	2.94
	2.56	2.75	2.94	2.56
	2.81	2.81	2.88	3.19
	2.81	2.56	3.06	3.06
	3.06	3.13	2.81	3.38
	3.19	3.06	2.94	2.88
	3.06	2.69	2.69	2.94
	2.94	2.94	3.19	2.63
	2.75	2.94	2.63	3.25
Average	2.88	2.91	2.89	2.92

---

[1] It was found impossible to obtain consistent results using hand mixing for the reason that it is never mixed twice alike, the gluten being unequally developed. The machine, No. 7223, of 10 to 12 lbs. capacity, was made by The J. H. Day Co., Cincinnati, Ohio.

TABLE II

Kind of Fat	Unhydrogenated [illegible] Oil			Hydrogenated [illegible]		
Date of baking	Dec [illegible]	Dec [illegible]	Dec [illegible]	Dec 1[illegible]	Dec [illegible]	Dec [illegible]
Date of test	[illegible]	[illegible]	Dec [illegible]	Dec [illegible]	Dec [illegible]	Dec [illegible]
Temp. of dough, °F	[illegible]	[illegible]	[illegible]	80	[illegible]	[illegible]
Temp. of room, °F	76	72	80	80	[illegible]	[illegible]
Temp. of oven, °F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Humidity, per cent	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Breaking Strength, Lbs.					
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
High	3 88	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Low	3.50	3 13	3 13	2 94	2 88	2 88
Average	[illegible]	[illegible]	[illegible]	[illegible]	3 21	[illegible]

It is obvious that there are no great differences in the individual cakes. The general averages check very closely. An accuracy of 1 to 2 per cent is readily attainable.

After the conditions have been standardized it is not necessary to use more than thirty cakes for each test.

Similar series with other oils, unhydrogenated and hydrogenated, seem to show that hydrogenation results in greater shortening power. Measurements have been made of the shortening power of the following oils and fats:

Lard
Lard compound
Butter
Cottonseed oil
Cottonseed oil, hydrogenated
Coconut oil
Coconut oil, hydrogenated
Corozo (cohune nut) oil
Corn oil
Olive oil
Peanut oil
Peanut oil, hydrogenated
Rapeseed oil
Soy-bean oil

In all the comparative breaking tests made on various oils and fats, lard is the best shortening agent; hence it is used as the standard. Its breaking strength will vary according to the conditions of standardization, and each operator must determine the value to be used as a standard.

The shortometer value in pounds is arbitrarily taken as 100 per cent. All other oils and fats having less shortening power will have a greater shortometer value. This weight in pounds of the standard divided by the weight in pounds of any other oil or fat will give its relative shortening value.

Experiments determining the crushing strength are not included in this article, but the same relationship holds.

CLASSIFICATION OF FLOURS

By holding all other ingredients constant and varying the flour used it is possible to arrive at a satisfactory classification of flours.[1]

A few results on flour are shown:

CLASSIFICATION OF FLOUR	BREAKING STRENGTH Lbs.
Soft winter	[illegible]
Soft winter	[illegible]
Soft winter	2 48
Soft winter	2 42
Medium winter	2 69
Medium winter	2 79
Medium winter	2 78
Strong winter	3 01
Strong winter	3 04
Strong winter	3 07
Spring	3 39
Spring	[illegible]
Spring	3 09

DEFINITION OF SHORTENING

That cake which requires the least load to measure its breaking strength is the shortest, that which requires the heaviest load is the least short.

The best shortening is that material which when baked in a dough gives to the product a minimum breaking strength and a minimum crushing strength.

SUMMARY

1—Apparatus has been devised which will measure the shortening value of different oils and fats and mixtures of them.

2—Shortening has been defined in terms of measurable units.

3—Lard has been found to be the best shortening agent.

4—Partial hydrogenation of an oil increases its shortening power.

5—A method has been suggested whereby flours may be classified.

---

[1] Further work is being done along this line.

A Process for Producing Palatable Sirup From Sugar Beets[1]

By Sidney F. Sherwood
OFFICE OF SUGAR-PLANT INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

The *Sugar Beet* (October 1906) refers to the very objectionable flavor and odor of sirup prepared from sugar beets and states that during the preceding fifty years numerous experiments had been made to eliminate this, but that all of the processes suggested were worthless. The same journal (January 1908) contains a brief note stating that "excellent" sirup is made from beets in Belgium and Germany by cooking the beets in water for several hours, pressing out the juice and evaporating directly to sirup of about 75 per cent solids; the statement is made also that about 70 g. of sulfuric acid are added to the extract from 100 k. of beets.

In 1917, C. O. Townsend and H. C. Gore[2] described a process, the essentials of which consisted in reducing the beet roots to thin slices, extracting the sugar by means of hot water, drawing off the sugar solution from the beet chips, and subjecting it to slow and long continued boiling and constant removal of scums during the process of evaporation. Acceptable sirup could be produced by the process recommended, but in a great many cases the odor and flavor was highly objectionable, while the sirup was always very dark in color. In January 1919, the writer suggested improvements in the process, the use of which resulted in marked improvement in the quality of the sirup produced. These suggestions were attached in printed form to copies of the bulletin sent out thereafter, and included thorough ripeness of the beet, removal of the top and upper green colored portions, removal of the skin, permitting the slices to fall directly into water of sufficient depth to prevent access of air and consequent oxidation and darkening of the slices, and direct evaporation to sirup.

John M. Ort and James R. Withrow, who investigated the preparation of beet sirup, were unacquainted with the fact that this improved process had been offered at the time they presented the results of their investigations before the Division of Industrial and Engineering Chemistry at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919, but refer to it in their published article,[1] and state that the precautions used are similar to those used by them and that the results obtained should be better than in the case of the original method. They tried many chemical and mechanical processes for clarification and removal of objectionable odor and flavor and state that none of them resulted in marked improvement in flavor. Identical results have been obtained by the writer in using many similar processes, and it is concluded that it is not advisable to suggest chemical processes at all for use where the sirup is to be produced upon a small scale, and that any mechanical processes suggested should be of the simplest sort. Ort and Withrow conclude that various published processes for making palatable sugar beet sirup do not consistently fulfil all claims made for them, that the sirup should not be evaporated in copper kettles, that, in the case of immature beets, the flavor will be improved by preliminary storage, etc.

---

[1] Received June 6, 1921.

[2] "Sugar Beet Sirup," U. S. Department of Agriculture, *Farmers' Bulletin*, 823 (1917).

[1] THIS JOURNAL, 12 (1920), 154.

Improved Process

The frequently occurring unpleasant and objectionable odor and flavor of beet sirup made by the original process is quite similar to that of beet molasses, though, of course, very much less pronounced. While the use of the modifications noted above resulted in marked improvement in the characteristics of the sirup, the objectionable odor and flavor was not always entirely absent and the work has been continued at intervals. Noting that beet molasses is a product resulting from the evaporation of juices and sirup under reduced pressure, it was considered that the characteristics of the sirup might be improved by some process of heating under pressure, and many experiments were made relative to processes of blowing air, steam, and superheated steam through juice, semi-sirup, and finished sirup; heating juice, semi-sirup, and finished sirup under pressure and at temperatures greater than the normal boiling point of finished sirup (105.5° to 106.5° C.), etc. As a result, the following process, for which a government patent[1] has been issued and the use of which is free to any citizen of the United States, was developed early in 1920, and is suggested as one affording the production of a satisfactory sirup from sugar beets: The beets are washed and the tops, upper green portions, and skin or peel removed. The beets are sliced, permitting the slices to fall directly into warm water of sufficient depth (an excess is avoided) to prevent access of air to the slices, heated to about 80° C. for about an hour, and the extract drained off and strained to remove fine particles, etc. This extract, or a similar extract prepared in any other manner, is placed in an autoclave—or other container which may be sealed—provided with a controlled outlet for blowing off steam and ordinarily with a pressure gage and thermometer, heated to 108° to 110° C. —corresponding to a pressure of approximately 21 lbs. to the sq. in.—and maintained at this temperature for 1 hr., blowing off a considerable quantity of steam at approximately 15-min. intervals. The extract is strained to remove the slight quantity of coagulated material and evaporated directly to sirup, removing the very slight amount of scum that forms.

Ordinarily this treatment serves to remove the objectionable odor and flavor, though the temperature, length of time of heating, and intervals for blowing off steam are not necessarily confined to the ones mentioned, but may be varied. Thus, in a number of instances, successful results have been obtained by heating to 110° to 112° C. for 0.5 hr. with constant blowing off of steam, the sirup in every instance being of a lighter color than those from a heating period of 1 hr. Sirups from a second extraction of the slices were quite acceptable, though they possessed a somewhat stronger flavor and their appearance was somewhat inferior.

Numerous lots of sirup have been prepared by the process from beets grown in southern Michigan and in each case the characteristics were satisfactory in that they were of an amber color, the unpleasant odor and flavor were absent, and the cloudiness was no greater than in average cane or sorghum sirup. (In several cases the sirup was perfectly clear.) Sirups such as cane, sorghum, maple, etc., possess characteristic flavors, and the after-taste of any one of them may be disagreeable to a person who is accustomed to any other one. Beet sirup possesses a flavor quite distinct from any other sirup, the first taste being agreeable and very sweet, while the after-taste is faintly similar to that of hoarhound, and expressions of opinion from numerous persons indicate that, as in the case with other sirups, it is agreeable to some persons and not agreeable to others.

Yield and Composition of Sirup

The yield of sirup varies, depending upon the sugar content of the beets. In the experimental work, the yield from 100 lbs. of beets averaged slightly over 2 qts. for a single extraction, and 1 qt. for a second, or a total of slightly over 3 qts. The beets were sliced with a large knife, and a somewhat larger yield would undoubtedly have been obtained with a slicing machine affording thinner slices. The debris (top, peelings, etc.) amounted to 40 to 50 per cent of the weight of beets. This material, and also the extracted slices, affords a valuable food for cattle, chickens, etc. The evaporation was continued until the boiling point reached 105.5° to 106.5° C., the thermometer not being permitted to touch the bottom of the evaporating vessel. The following is the composition of a number of sirups:

Composition of Beet Sirup

Sample No.	Sucrose Clerget HCl Cold Per cent	Reducing Sugars (As Invert Sugar) Per cent	Ash Direct (Not as Carbonate or Sulfate) Per cent	Total Solids (Refractometer) Per cent	Undetermined Per cent
1	61.53	3.43	1.39	69.92	3.57
2	61.07	3.32	1.54	68.87	2.94
3	62.38	2.43	1.20	68.37	2.36
4	63.68	3.10	1.13	70.87	2.96
5	63.98	3.01	1.52	71.82	3.31
6	63.06	2.60	1.56	70.87	3.65
7	65.28	2.39	1.33	71.77	2.77
8	64.60	1.54	1.25	69.82	2.43
Average	63.20	2.73	1.37	70.29	3.00

Application to Home Production of Sirup

The object of these investigations has been directed entirely to processes for the production of palatable sirup from sugar beets on a small scale, as in the home, and the heating may be carried on in a very satisfactory manner in the ordinary pressure cookers used in a great number of homes. In fact, one of these cookers was used frequently for preparing the experimental sirup. With beets at $7 per ton, the cost of 100 lbs. would amount to only 35 cents, and sirup could be produced at small cost if, as in the case in the home, the value of time and labor were not included. It is considered not improbable that at some time beet sirup may be produced profitably on a factory scale—utilizing the by-products as cattle feeding material—especially in certain sections of the West, admirably suited for the production of beets but situated far from a beet-sugar factory and in which the available agricultural land is insufficient to support such a factory. In this connection it is worthy of note that the consumption of beet sirup in Germany in 1916 to 1917 amounted to 20,000 tons (probably metric).[1]

Decolorizing

In connection with the study of the process, experiments were made to ascertain the effect of infusorial earth and decolorizing carbon. The treatment of hot semi-sirup containing 45 to 50 per cent solids with 3 per cent of its weight of infusorial earth, filtration under pressure, and direct evaporation to sirup resulted in sirup of an improved degree of clearness as compared with untreated sirups. Treatment of the filtrate with decolorizing carbon resulted in sirup of somewhat lighter color, but the differences between these sirups and sirups from treatment with infusorial earth alone were not great. Obviously such processes would not be practical for use in small-scale operations, though they would probably prove advantageous in the case of factory production.

---

[1] U. S. Patent 1,370,372 (March 1, 1921), Sidney F. Sherwood.

[1] Berthold Block, "Beet Sirup," Through *J. fabr. sucre.*, **61** (1920), 282.

The writer has not had an opportunity to consult the book by Berthold Block on beet sirup manufacture and use, but a review of it makes no mention of superheating processes, though a brief reference[1] to the manufacture in Germany of sirup from beets states that coarse pieces of beets are treated with steam at 100° to 104°C. for 3 hrs., resulting in removal of bad odor and flavor and the development of a flavor of vanilla. Subsequent to working out the above process, the writer became acquainted with a patent issued to H. S. Alexander[2] covering a process for producing an "edible" sirup from sugar beets in which the beets are cooked before pulping for 0.75 to 1.5 hrs., preferably by steam under pressure and at a temperature of 110° to 130° C., shredded, pressed, and the juice filtered and evaporated to sirup; and also one issued to P. Kestner[3] covering a process for evaporating beet juice in an evaporator until sirup of the desired concentration has been produced and then heating under pressure for a very brief period to remove objectionable odor and flavor. As an example, he states that sirup that would boil at 120° C. under atmospheric pressure is heated under pressure until the temperature reaches 130° C., more or less, and the sirup is then cooled at once by releasing the pressure. He states that it can be maintained at this high temperature for a few seconds only or the sirup will be caramelized (burned). The writer's process is believed to be more satisfactory than either of these, in that the introduction into the extract of semi-soluble and suspended material from cooked and pulped beets is avoided and actual filtration is rendered unnecessary, while the danger of scorching is eliminated.

CONCLUSIONS

1—A simple and satisfactory process is described whereby the objectionable odor and flavor of beet sirup is eliminated and a palatable sirup produced.

2—The composition of several sirups is given.

A Study on the Oil Bromide Test of Linseed Oil[1]

By Thomas A. Davidson

31, Eastbourne Gardens, Monkseaton, Northumberland, England

The valuation of linseed oil as a drying oil is still carried out by indirect methods. The iodine value test estimates constituents of a nondrying nature, as well as those imparting drying properties to the oil. The hexabromide test applied to the oil, as described by Hehner and Mitchell,[5] would seem to have fallen into desuetude, whereas renewed attention has from time to time been given to the test as applied to the separated fatty acids. Lewkowitsch[6] would appear to have set the fashion by stating that after "very extensive practice it is preferable to apply this test to the isolated fatty acids."

The drying properties of linseed oil are due to the glycerides of linolenic acid, and not to linolenic acid itself.

The attention given to the hexabromide test upon the isolated fatty acids has no doubt been due to the assumption that linolenic acid was present in linseed oil as the simple glyceride, trilinolenin, to which it bears a simple relationship. There is good reason for doubting that linolenic acid is present as a simple glyceride, as the evidence which the author has to put forward suggests that it exists in linseed oil as a mixed glyceride. On this account, and until the composition of the linolenic glycerides has been placed beyond doubt, it is desirable that the test be applied to the oil direct, and not to the isolated fatty acids. After considerable work on the insoluble bromoglycerides, the author is satisfied that the chief reason for comparative disuse of the hexabromide test since Hehner and Mitchell's paper appeared has been the difficulty of obtaining the bromo derivative as a clean, free powder, when dried.

To differentiate between the two tests it is proposed to use the term "oil bromide" for the insoluble brominated glycerides, and "hexabromides" for the insoluble brominated acid, hexabromostearic acid.

While it is desirable that the oil bromide test should give the full theoretical yield of the linolenic glyceride derivative, such a result—depending as it does on differential solubilities—appears so far to be impracticable. It is of greater importance that the test, carried out under specified conditions, should be capable of giving consistent results in the hands of different workers and have only a small experimental error; and that the precipitate be of reasonably constant composition. The test proposed here should satisfy these conditions, and has the advantage of a considerable saving of time over the hexabromide test on the isolated fatty acids. It should not take much longer to carry out than the determination of the iodine value, but its results should prove of considerably greater value as an indication of drying power.

The oil bromide yields in this test are higher than any in the literature, and undoubtedly the proposed method applied to the poorer drying oils, such as hempseed and poppy-seed oils, will give higher results than any so far recorded for them.

The investigation whose results are now being presented was carried out in the intervals of routine work and other research work from 1907 to 1910, and is not as complete as the author would wish. Since that time, no opportunity of completing the investigation has offered itself, and the author considers it desirable, without delaying further, to place on record his results, which, giving an improved method of preparation, go far enough to point out the road to complete success for any further investigation.

PURPOSE OF INVESTIGATION

The purposes of the investigation where:

1—To find out what was wrong with the test as described by Hehner and Mitchell,[1] and the causes of the large experimental error.

2—To ascertain the most convenient method of separating the oil bromides from the reaction mixture.

3—To discover a means of separating the oil bromides as a loose, dry, granular powder.

4—To determine the most reliable and convenient method for the estimation of bromine in the oil bromides.

5—To gain some information as to their properties and composition.

6—To formulate the most suitable working conditions to insure maximum yield and maximum purity.

---

[1] J. fab. sucre., 61 (1920), 25.1.

[2] Brit. Patent 133,744 (October 13, 1919).

[3] Brit. Patent 135,235 (November 27, 1919).

[4] Received January 11, 1921.

[5] ANALYST, 23 (1898), 310.

[6] Chemical Technology o fOils, Fats and Waxes, 1909, I, 384.

PRELIMINARY EXPERIMENTS

In preliminary work on varnish linseed oils, Hehner and Mitchell's method was used.

From 1 to 2 g. of oil were dissolved in 40 cc. of ether, and 5 cc. of glacial acetic acid were added. The mixture was cooled in an ice bath to 0° C., and carefully brominated, using enough excess bromine to give a distinct reddish color. After 3 hrs. at 0° C. the precipitate was separated, washed with three 10-cc. lots of ether, and dried to constant weight.

Whereas Hehner and Mitchell obtained yields of only about 24 per cent, with a single instance of 42 per cent, the yields obtained by the present writer were generally over 50 per cent. Great difficulty was experienced in separating the precipitate and washing it satisfactorily because of the volatility of the ether. Filtration through a Gooch crucible with slight suction was first tried, but it was found that the oil crept to the top of the crucible; that the resulting washed product dried hard and horny, although the precipitate had been granular and that it was difficult to dry to constant weight. Filtration through an inverted thistle funnel covered with chamois leather offered no advantage. Following the experience of L. M. Tolman,[4] a centrifuge was tried for the separation and washing of the precipitate. The resulting manipulation proved much simpler, and this method was finally adopted. The most suitable form of apparatus proved to be as shown in the figure: *a* is a thin, round, flat-bottomed glass tube 6 in. long by 1 in. in diameter, fitted with a sound cork, *b*, through which passes a thin glass rod, *c*, which can be used for stirring the oil solution during bromination, and for breaking up the precipitate for washing. The complete apparatus need not weigh more than 25 to 30 g. Any type of centrifuge taking these tubes may be used. In the present experiments a geared-up, hand-driven model was used. To minimize breakage of tubes, a thin slice of cork is fitted at the bottom of each metal tube in the centrifuge, for the bottom of the glass tube to bear against. Glass tubes, corks, and rods should be carefully selected of practically equal weight, so that the weights in centrifuge tubes are equally balanced.

A summary of the results of these experiments is given in Tables I, II, and III. In all cases the amount of oil stated in the tables was dissolved in 40 cc. ether, with or without acetic acid. It was cooled before and during bromination, and was finally washed three times with 10 cc. each of ether or the solvent used in test, unless otherwise stated. The use of acetic acid was recommended by Hehner and Mitchell as yielding a more granular precipitate.

CONCLUSIONS FROM EXPERIMENTS—(1) Acetic acid in the solvent results in a reduced yield, as is indicated by a comparison of Tests 1 to 4 with Tests 5 and 6 in Table I, and of Tests 6 to 12 with Test 14 in Table III.

(2) An increased ratio of oil to solvent gives an increased yield, as is seen by comparing Tests 2 and 3 in Table III with Tests 4 to 12 and 14, and with Tests 15 and 16 in the same table.

In seeking for the causes of the large experimental error, the condition of the dried oil bromide was held partly responsible. It was observed that although the oil bromide was in a granular condition during precipitation and washing, it was obtained as a horny mass, hard and tough, and of slightly softer consistency below the surface. This suggested that the oil bromide was soluble in the ether, which on evaporation deposited the solute as a varnish film, cementing all the particles together.

TABLE I—OIL BROMIDES [illegible] LINSEED OILS

No.	Ref. No. of Oil	Oil to 40 Cc. Solvent, Grams	Yield Oil Bromides, Per cent	Average, Per cent	Containing Br. Per cent	Remarks
1	233	1.005	[illegible]	[illegible]	56.24	Solvent ether + 7.5 per cent acetic acid
2	[illegible]	1.022	41.68			
3	[illegible]	1.023	[illegible]		57.45	Solvent ether + 7.5 per cent acetic acid
4	233	1.031	38.55			
5	233	1.018	42.93	[illegible]	58.16	Solvent ether only
6	[illegible]	[illegible]	43.15			
Average			40.86	[illegible]		

TABLE II—OIL BROMIDES FROM CALCUTTA LINSEED OILS

No.	Ref. No. of Oil	Oil to 40 Cc. Solvent, Grams	Yield Oil Bromides, Per cent	Containing Br. Found, Per cent	Average, Per cent	Remarks
1	[illegible]	1.976	[illegible]			
2	176	1.822	49.00			
3	31	1.741	[illegible]			
4	[illegible]	2.138	53.24	57.37		
5	[illegible]	2.144	53.31	57.50	57.43	
6	202	1.006	46.82			
7	202	1.009	47.47			
8	202	1.015	46.80	57.94		
9	202	1.898	55.90	57.83	57.89	
10	[illegible]	2.373	49.90			
Average			50.85	57.66		

TABLE III.—OIL BROMIDES FROM BALTIC LINSEED OILS

No.	Ref. No. of Oil	Oil to 40 Cc. of Solvent Grams	Bromides Found	Yield Oil Aver., Per cent	Aver., Per cent	Containing Br. Found Aver., Per cent	Remarks
1	[illegible]	2,273	60.0				Svy. ether 40 cc. + acetic acid 3 cc.
2	[illegible]	[illegible]	49.3	49.8	57.50		Washings 1, acetic acid 5 cc.
3	[illegible]	0.543	[illegible]				Washings 2, alcohol 5 cc.
							Washings 3, ether 5 cc.
4	[illegible]	0.992	61.7	61.7			Do., do.
5	[illegible]	1.000	61.7				
6	[illegible]	1.012	50.3	50.2			Svt. ether (0.717) + 7.5% acetic acid 40 cc.
7	[illegible]	1.010	[illegible]				
8	[illegible]	1.038	50.9				Washings 1, solvent Washings 2, ether (0.717) Washings 3, ether
9	50	0.999	[illegible]		58.69	Over	Svt. ether (0.725) + 7.5 [illegible] acid 40 cc.
10	50	1.001	52.7	52.5	58.50	58.55	
11	50	1.007	51.1				Washings 1, solvent
12	50	1.021	[illegible]				Washings 2, ether (0.725) Washings 3, ether (0.725)
13	50	1.245	59.6				Svt. ether + 7.5 acetic acid 40 cc.
14	50	1.003	56.9			58.60	Ether alone
							Svt. ether
15	50	2.008	66.5	65.6			Washings, 3 × 15 cc. ether
16	50	2.011	[illegible]				Svt. ether (0.725) +
17	293	2.007	67.7	67.5			0.2% acetic acid
18	293	2.009	67.3				Washings, 3 × 10 cc. ether (0.725)
19	293	2.012	72.3	72.3			Svt. ether (0.717) + 0.2% cetic acid
20	293	2.015	72.3				Washings, 3 × 10 cc. ether (0.717)
21	297	2.025	[illegible]	72.2			Svt. ether (0.725) +
22	297	2.011	72.4				0.2 [illegible] acid Washings, 3 × 10 cc. ether (0.725)
23	297	2,023	73.7	73.6			Svt. ether (0.717) +
24	297	1.995	73.4				0.2% acetic acid Washings, 3 × 10 cc.
Average			60.9			58.30	ether (0.717)

SOLUBILITY TESTS

Saturated solutions were made by warming together 2 g. of an average sample of crude oil bromides with 50 cc. of solvent, keeping the corked flasks immersed in a bath of water at 60° F. for 1 day, and filtering through paper. Twenty cc. of filtrate were evaporated in small aluminium basins to constant weight. The following results were obtained:

SOLVENT	[illegible]	GRAMS PER LITER
Ether (sp. gr. 0.717 at 15.5° C.)		6.8
Ether (sp. gr. 0.725 at 15.5° C.)[1]	0.134	6.7
[illegible]	0.002	[illegible]
[illegible]	0.143	7.15
Ether (0.725) + alcohol (90:10)	0.117	[illegible]

[1] [illegible]

[2] Grain alcohol, 90 per cent; wood naphtha, 10 per cent.

The insolubles left on the filter paper from the ether had set to horny masses; those from ether and alcohol mixtures were not quite so hard; while those from alcohol alone were quite a free powder. This latter fact, coupled with the low solubility of the oil bromides in alcohol (1 part in 10,000), at once suggested the use of alcohol as a final wash liquor to remove the ether from the washed oil bromide. A marked improvement was the result. The bromide was obtained as a nice, free powder, and it was felt that the experimental error due to differences in drying had been overcome.

ESTIMATION OF BROMINE

Before the bromine in the oil bromides can be estimated it is necessary to convert it into a soluble form which will react with silver nitrate to form the insoluble silver bromide, after which its treatment may be either gravimetric or volumetric. The following methods were tried:

(1) IGNITION WITH LIME—The oil bromide was intimately mixed with lime in a platinum crucible and covered with a good layer of lime. This was heated gently at first, then more strongly. After cooling, the mass was dissolved in a slight excess of nitric acid, and filtered. In gravimetric determinations, the silver bromide precipitate should be allowed to stand in the dark overnight; otherwise results tend to be high. If filtered off soon after precipitation, the silver bromide retains traces of calcium salts.

(2) IGNITION WITH LIME AND CARBONATE OF SODA—The comment on Method 1 applies also to this case.

(3) IGNITION WITH LIME AND SODIUM PEROXIDE, according to Parr.[1] The reaction in this case was too vigorous, and there was risk of loss.

(4) SAPONIFICATION WITH ALCOHOLIC POTASH—This could be made a satisfactory method if saponification were complete and definite, but as shown under the heading "saponification" this is questionable.

(5) SAPONIFICATION WITH SODIUM ETHOXIDE, prepared *in situ*.[2,3,4] This was the most reliable and rapid method of all. Careful attention must be given to maintaining constant the ratio of oil bromide to alcohol and to sodium. The ratio employed in the present work was:

W = grams oil bromide (0.2 to 0.3 g.)
68 W = Cc. alcohol (not under 98 per cent)
8.5 W = grams fresh metallic sodium

This mixture was heated under a reflex condenser, and over a very tiny flame for 1 hr. Treated in this manner, the reaction product was very thick when cold. There was no spitting. The product was practically colorless, and on addition of dilute nitric acid a very peculiar, hardly pleasant odor was noticeable. There was only a very small separation of solid fatty bodies. Volhard's method[5] was used for the volumetric estimation. A known excess of 0.1N silver nitrate was added, and the excess was titrated back with 0.3N ammonium thiocyanate in the presence of a ferric salt. An accuracy of 0.1 per cent was possible.

COMPARATIVE TESTS OF METHODS—A comparison of Methods 1, 4, and 5 was made upon a sample of crude oil bromides prepared from a Baltic linseed oil. Its melting point was low, about 116° C.

	DETERMINATION	PER CENT BROMINE
Method 1	Gravimetric	55.69
	Volumetric	55.92
Method 4	Gravimetric	56.25
	Volumetric	56.00
Method 5	Volumetric	57.02

After considerable experiment, the last-named method was considered the most reliable, giving total conversion of bromine into a soluble form without any possible loss during conversion. Consistently higher results were always obtained with Method 5 than with Method 1, and it was questioned whether Method 1 gave absolutely accurate results. It is of interest to compare the bromine content as found by Hehner and Mitchell. Their results varied from 55.55 to 56.38 per cent, an average of 56.12 per cent. The present writer's results by the lime method generally ran from 56.2 to 57.5 per cent, whereas by the Stepanow-Bacon method they were generally over 57.5 per cent. The variations cannot be entirely due to variations in composition. Most of the figures for bromine content in Tables I, II, and III were determined by the lime method, and the results are not considered so accurate as those in Tables VI and VII, which were determined by the Stepanow-Bacon method. In a private communication Mr. C. A. Mitchell informs the author that the method of ignition with lime in a combustion tube was used in their determinations of bromine. As tending to confirm the unreliability of the lime ignition method, reference may again be made to Hehner and Mitchell's paper. Purified samples of hexabromostearic acid of melting point 180° to 181° C. were found to contain 61.38 to 61.80 per cent bromine (theory 63.31 per cent Br). Again, a several times recrystallized sample of tetrabromostearic acid of melting point 113.4° C. was found to contain only 51.97 per cent bromine (theory 53.32 per cent). These differences from theory equal 2.7 and 2.4 per cent, respectively.

ACTION OF ALCOHOLIC POTASH

Alcoholic potash acts not only by saponifying the glyceride, but by abstracting the bromine from the molecule, forming potassium bromide. The following experiments were originally undertaken in the hope that the saponification value would serve as a substitute for the bromine determination, as a check on the composition of the oil bromides. Half-normal alcoholic potash was first tried. The salts produced being insoluble in alcohol, the reaction mixture was very liable to spit up during heating. Long-necked Kjehdahl flasks were used, tilted, and connected to upright condensers by means of bent adapter tubes, so that any salts spitting up would remain within the flask. Spitting was so bad that it was found advisable to add a few cubic centimeters of water to dissolve the salts. Normal alcoholic potash made up in 90 per cent alcohol was next tried. This gave higher saponification values, but, as can be seen from Table IV, the figures were indefinite. The maximum value, 482.7, was reduced on further heating to 469.0. Blank tests were run alongside the regular tests for the same times.

TABLE IV—SAPONIFICATION VALUES OF OIL BROMIDES

Time of Heating Hours	Saponification Value 0.5 N Alc KOH	Saponification Value 1.0 N Alc KOH	Time of Heating Hours	Saponification Value 0.5 N Alc KOH	Saponification Value 1.0 N Alc KOH
0.5	441.6		2.5	..	482.7
1	446.2	464.3	3	.	470.7
2	.	471.5	4	....	469.0

The figures given in Table IV are the average of a large number of tests. In Table V will be found the saponification values of each of the possible unsaturated glycerides up to linolenin. The values are calculated on the assumption that for saponification with complete removal of bromine, the number of molecules of potassium hydroxide required equals the number of atoms of bromine in the molecule of oil bromide plus 3 (for saponification).

ACTION OF SODIUM ETHOXIDE PREPARED *in situ*

Sodium ethoxide, prepared *in situ*, removes the bromine

---

[1] *J. Am. Chem. Soc.*, **30** (1908), 68; *C. A.*, **2** (1908), 1802.
[2] Stephanow, *Ber.*, **39** (1906), 4056.
[3] Rosanoff and Hill, *J. Am. Chem. Soc.*, **29** (1907), 269.
[4] Bacon, *J. Am. Chem. Soc.*, **31** (1909), 49.
[5] Treadwell and Hall. "Analytical Chemistry," 1909, II, 545

TABLE V—POSSIBLE BROMINATED GLYCERIDES OF THE UNSATURATED ACIDS PRESENT IN LINSEED OIL

Name	Formula	Mol. Wt.	Sap. Value	Percentage Composition C	H	O	Br
Trilinolenin bromide or hexabromostearin	$(C_{17}H_{29}Br_6COO)_3\ C_3H_5$	2312	509.5	29.58	3.98	4.15	62 28
Dilinolenin-linolin bromide	$\begin{matrix}(C_{17}H_{29}Br_6COO)_2\\(C_{17}H_{31}Br_4COO)\end{matrix}\rangle C_3H_5$	2154	494.9	31.76	4.35	4.46	59.4
Dilinolenin-olein bromide	$\begin{matrix}(C_{17}H_{29}Br_6COO)_2\\(C_{17}H_{33}Br_2COO)\end{matrix}\rangle C_3H_5$	1996	477.8	34.27	4.81	4.81	56.11
Linolenin-dilinolin bromide	$\begin{matrix}(C_{17}H_{29}Br_6COO)\\(C_{17}H_{31}Br_4COO)_2\end{matrix}\rangle C_3H_5$	1996	477.8	34.27	4.81	4.81	56.11
Linolenin-linolin-olein bromide	$\begin{matrix}(C_{17}H_{29}Br_6COO)\\(C_{17}H_{31}Br_4COO)\\(C_{17}H_{33}Br_2COO)\end{matrix}\rangle C_3H_5$	1838	457.8	37.21	5.33	5.23	52.23
Trilinolin bromide or tetrabromostearin	$(C_{17}H_{31}Br_4COO)_3\ C_3H_5$	1838	457.8	37 21	5 33	5 23	52 23
Linolenin-diolein bromide	$\begin{matrix}(C_{17}H_{29}Br_6COO)\\(C_{17}H_{33}Br_2COO)_2\end{matrix}\rangle C_3H_5$	1680	434.1	40.72	5.95	5.71	47.62
Dilinolin-olein bromide	$\begin{matrix}(C_{17}H_{31}Br_4COO)\\(C_{17}H_{33}Br_2COO)_2\end{matrix}\rangle C_3H_5$	1680	434.1	40.72	5.95	5.71	47.62
Linolin-diolein bromide	$\begin{matrix}(C_{17}H_{31}Br_4COO)\\(C_{17}H_{33}Br_2COO)_2\end{matrix}\rangle C_3H_6$	1522	405.5	44.94	6.70	6.31	42.05
Triolein bromide or dibromostearin	$(C_{17}H_{33}Br_2COO)_3\ C_3H_5$	1364	370.2	50 15	7 62	7 04	35 19

easily and completely. Oil bromides treated by the Stepanow-Bacon method formed a thick reaction product, and there was no loss of material by spitting. When acidified, it was observed that the fatty bodies which separated were solid, not liquid. It is presumed that the nascent hydrogen not only removed bromine, but reduced the unsaturated acids to stearic acid. No experiments were carried out to verify this, though only an iodine value determination of the separated fatty acids would be required. It is probable that the following reactions take place at the same time:

$(C_{11}H_{29}Br_1.COO)_2 = C_3H_5 + 32\ H = (C_{17}H_{35}.COO)_3C_3H_5 + 16HBr$
$(C_{17}H_{31}Br_4\ COO)$— Stearin (1)
Dilinolenin-linolin Bromide

$$EtONa + HBr = NaBr + EtOH \qquad (2)$$

$(C_{17}H_{35}COO)_3.\ C_3H_5 + 3\ EtONa = 3\ C_{17}H_{35}.COO\ Na + C_3H_5(OEt)_3$ (3)
Stearin Sodium Stearate Triethylin

MELTING POINT OF OIL BROMIDES

A number of determinations showed that the melting point was not sharp, which indicated that the oil bromide was not a pure substance. It softened at 130° C., liquefied about 140° to 145° C., and darkened at higher temperatures. A sample recrystallized from carbon tetrachloride melted at 151° (corr.). Hehner and Mitchell give the melting point of their oil bromides as 143.5° to 144° C.

PROPERTIES OF THE CRUDE OIL BROMIDE

Crude oil bromide is an amorphous solid of faintly yellow color, odorless, stable at moderate temperatures, melts at 140° to 145° C., hardening to a waxy solid on cooling, and decomposes on stronger heating. It contains approximately 57 to 58 per cent bromine, and, when moist, decomposes readily in contact with iron (*e. g.*, a spatula) with liberation of bromine. It is moderately soluble in chloroform, carbon tetrachloride, acetone, and acetic acid, slightly soluble in benzene, petroleum ether, and ether, and practically insoluble in alcohol. It is saponified by sodium ethoxide with removal of bromine, and is also saponified by alcoholic potash with removal of bromine, but much less easily. The oil bromide is not a pure substance, but appears to be of fairly uniform composition, depending upon the conditions of preparation.

PURIFICATION OF CRUDE OIL BROMIDES, CONTAINING 57.10 PER CENT BROMINE

Several attempts were made to purify the oil bromide by crystallization. In all the solvents tried, there seemed to be only a slight difference in solubility between the higher bromide and its accompanying lower bromide.

ETHER—The ether-soluble portion had a melting point below 100° C. and contained 55.36 per cent bromine.

CARBON TETRACHLORIDE—A saturated solution of crude oil bromides in hot carbon tetrachloride was filtered hot and allowed to crystallize. The separated precipitate was whirled and washed several times with a mixture of ether and alcohol (2:1), and finally washed with alcohol alone and dried. The crystallized product was almost pure white in color, melting point 151° C., and contained 59.24 per cent bromine. The substance separated from the mother liquor was waxy and tough, but not hard. It contained 55.62 per cent bromine.

ACETONE—Five grams of crude oil bromide were heated with 250 cc. of acetone and filtered. A portion (0.36 g.) which remained undissolved was washed with alcohol and dried. It tested 58.09 per cent bromine. The filtrate was slowly cooled by immersing the flask containing it in a bulk of water at 99° C., which was allowed to cool gradually. The crystalline precipitate was washed in succession with acetone and alcohol and dried. The yield was 1.63 g., and the bromine content was 58.04 per cent. (These recrystallization experiments were interrupted and unfortunately were never completed.)

Various solvents were tried, and the bromine content of the first crop of crystals was estimated, as summarized in the following results:

	Per cent Br.		Per cent Br.
Carbon tetrachloride	59.24	Benzene and ether (1:1)	58.17
Benzene and alcohol (1:1)	58.43	Benzene	57.74
Acetone	58.04	Acetic acid	57.38

COMPOSITION OF OIL BROMIDE

Table V contains a list of the possible glycerides of the unsaturated acids up to linolenic acid, with their calculated percentage composition. It will be observed that the bromine content is likely to give quite as much information as the estimation of carbon and hydrogen.

Hehner and Mitchell suggested tentatively that the composition was dilinolenin-olein bromide, basing their conclusion upon an ultimate analysis, and an average of a number of bromine estimations, 56.12 per cent. They seem to have overlooked the fact that linolenin-dilinolin bromide has also exactly the same percentage composition and also contains 56.11 per cent bromine.

Gemmell[1] considers the composition to be a varying mixture (according to conditions of preparation) of tetrabromostearin and hexabromostearin.

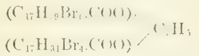
Tetrabromostearin is very easily soluble in ether, so that it is unlikely to be precipitated from an ether solution of oil. It ought also to be comparatively easy to separate the tetra- and hexabromostearins by the action of solvents. In the present recrystallization experiments the maximum.

---

[1] [illegible]

bromine percentage obtained (on a sample recrystallized from carbon tetrachloride) was 59.24 per cent bromine. Both these figures are a good way removed from hexabromostearin (theory 62.28 per cent) and tetrabromostearin (theory 52.23 per cent).

In the writer's opinion it is unlikely that the composition is that of a mere mixture of hexabromostearin and tetrabromostearin. It seems more probable that the composition is mainly dilinolenin-linolin bromide (theory 59.42 per cent



$$\begin{matrix}(C_{17}H_{29}Br_6.COO)_2 & \\ & C_3H_5 \\ (C_{17}H_{31}Br_4.COO) & \end{matrix}$$

bromine), admixed with some (unidentified) brominated glyceride of lower bromine content. It is not improbable that any mucilage in the raw oil is also carried down by the precipitated oil bromides. In the crystallization experiments, the solutions were generally hazy and required filtration.

The glycerides from which the bromo derivatives in Table V are formed are practically unknown compounds. It would be very interesting to know the comparative drying value of all the glycerides containing linolenic acid. Future investigation on these lines is very desirable.

FURTHER EXPERIMENTAL WORK

Profiting by the experience just recorded, a further series of tests were carried out on Baltic linseed oil, of iodine value 198.5 (Wijs, 2 hrs., 23°C.), varying the ratio of oil to solvent, using 40 cc. of chilled ether (sp. gr. 0.717) as solvent, washing the precipitate twice with 10 cc. of ether, and once with 10 cc. of alcohol. The results are given in Table VI. Bromine was estimated by the Stepanow-Bacon method. It can be seen that as the ratio of oil to solvent increases, the yield of oil bromide increases, and also that the bromine content remains fairly constant. If a graph be made from Table VII, of oil bromide yield and amount of oil taken, it will be found that the points do not form a smooth curve, which fact appears to indicate some differences in the solubility factor.

The mean experimental errors in the oil bromide yields in Table VI are respectively (from 1 to 5 g.) 0.55, 5.16, 1.22, 0.51, and 4.66 per cent. This variable error was considered to be due to the heating up of the tubes by the hand when the precipitate was broken up with ether for washing, thereby increasing the solubility factor of the oil bromide in ether. For this reason it is desirable to cool the tubes in the ice bath after breaking up the precipitate with the wash liquors.

There is just a possibility that some substitution of bromine may have taken place with the greater concentration (12.5 per cent) of the 5-g. tests. It is also possible that an additional ether wash would have given more agreement in the yields. The fact that the bromine content is so close to those of the other tests is compatible only with a greater amount of lower bromides in the precipitate, provided a certain amount of substitution had taken place.

These considerations were borne in mind in framing the proposed method of preparation.

TABLE VI—EFFECT OF OIL CONCENTRATION ON YIELD OF OIL BROMIDES

Nominal Wt. Oil Grams	Oil Used Grams	Oil Bromides Found Per cent	Oil Bromides Average Per cent	Containing Br Found Per cent	Containing Br Average Per cent	Color of Oil Bromide
1	[illegible]	63.25	63.6			Nearly white
	1.005	[illegible]				
2	2.000	65.30		57.80		
	2.002	[illegible]	65.1	58.03	57.98	Nearly white
	2.007	[illegible]		58.27		
	2.010	62.77		57.26		
3	3.009	71.02	71.9			Nearly white
	3.013	72.69				
4	4.011	70.70	71.1	57.91	57.93	Nearly white
	4.016	71.46		57.95		
5	4.991	78.08	81.9	[illegible]	[illegible]	Yellow
	5.005	85.71		57.37		

EFFECT OF HEATING UPON THE CONSTANTS OF LINSEED OIL

It is considered of interest to include Table VII, which shows the effect of heat upon the oil bromide yield and other constants of the same No. 50 Baltic linseed oil. Sample L863 was cooked in an open copper pot (*i. e.*, exposed to air) for 1 hr. at 260°C. (Loss, 1.43 per cent.) Sample L903 was cooked in a closed glass flask in an atmosphere of hydrogen for 4 hrs. at 260°C. (Loss, 0.83 per cent.) Expt. L863 was selected from a range of experiments because in specific gravity and refractive index it so closely resembled L903. It will be noted from the figures that the chemical reactions involved are markedly different, according as the heating takes place in the presence or absence of air.

TABLE VII—EFFECT OF HEAT UPON CONSTANTS OF BALTIC LINSEED OIL

Oil	Sp. Gr. $\frac{15.6°}{15.6°}$ C.	Oil Bromides G. Oil Used	Oil Bromides Yield Per cent	Acid Value	Saponification Value	I. V. Wijs 2 Hrs., 23°C.	Refractive Index 20.0°C.	Viscosity "Redwood" sec., 21.1°C.
Raw	0.9373	2.008	66.5	5.1	190.4	198.5	1.4822	206
		2.011	64.6					
		1.003	56.9					
L863	0.9413	0.998	20.2	3.3	190.5	187.7	1.4841	345
		1.006	20.5					
		1.008	19.5					
		1.014	20.5					
L903	0.9414	1.003	2.7	6.0	185.8	184.2	1.4842	428
		2.000	4.4					
		2.011	4.1					

SUGGESTED METHOD FOR OIL BROMIDE ESTIMATION

The method finally proposed is as follows: For the separation use centrifuge and corked tubes and rods, as described above. For solvent and washing use ether (sp. gr. 0.717) which has been saturated at 0°C. with a purified sample of oil bromide (obtained from preliminary experiments). Measure ether and alcohol (sp. gr. 0.820) at 0° to 5°C.

Dissolve 4.00 g. of linseed or other oil in 35 cc. of ether. Cool in an ice bath to 0°C. Add 1.0 cc. of bromine slowly from a 10-cc. stoppered buret, divided into 0.1 cc. and with the orifice constructed so that bromine is delivered slowly when tap is turned full on. While adding the bromine, stir the reaction mixture so as to avoid local rise of temperature. Wash down the top of the tube with 5 cc. of ether. Cork and let stand at 0° C. for 2 hrs. to insure complete bromination. There should be an excess of bromine present after 2 hrs. Whirl the tubes in the centrifuge for 3 min. at 2000 r.p.m. Decant liquor from precipitate. Wash down the tube and rod with 10 cc. of ether, break up precipitate with rod thoroughly, and cool in ice bath for a few minutes. Whirl as before for 3 min. at 2000 r.p.m. Decant liquid. Repeat washing with 10 cc. of ether as before. Cool, whirl, and decant. Give a final washing with 10 cc. alcohol, breaking up precipitate as before, cool, and whirl for 3 min. at 1600 r.p.m. Decant as before, and dry first in air, then in a hot-water oven for 0.5 hr.

PRECAUTIONS—The following precautions should be observed:

1—Keep all temperatures low.

2—Make all measurements carefully, especially of the ether, and weigh the oil to within 1 per cent of quantity stated.

3—Use ether saturated at 0° C. with oil bromide.

4—After breaking up the precipitate in wash liquor, always cool in ice bath before whirling.

5—After the alcohol wash, do not whirl at a greater speed than 1600 r.p.m. If a higher speed be used, the precipitate will pack together and be difficult to dry properly.

6—Avoid the use of acetic acid.

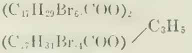
SUMMARY

1—The centrifuge was found to be the most satisfactory means of separating oil bromides from the reaction mixture, and the volatibility of ether proved no drawback.

2—Alcohol (sp. gr. 0.820) used as a final wash liquor removes ether, and yields oil bromides as a loose granular powder when dried.

3—The Stepanow-Bacon method was found to the most satisfactory and accurate of the methods tried for the estimation of bromine in oil bromides.

4—The properties of the crude oil bromide are summarized, and its composition is suggested to be mainly dilinolenin-linolin bromide



$$\left.\begin{matrix}(C_{17}H_{29}Br_6.COO)_2\\(C_{17}H_{31}Br_4COO)\end{matrix}\right\rangle C_3H_5$$

5—A method is given, based on the results of this investigation, which should ensure a maximum yield of oil bromide of maximum purity, and with small experimental error.

The Precipitation of Solid Fatty Acids with Lead Acetate in Alcoholic Solution[1]

By **E. Twitchell**
Wyoming, Ohio

If a hot alcoholic solution of a mixture of fatty acids, such as is obtained from an ordinary fat or oil, is treated with an alcoholic lead acetate solution, also hot, there is no precipitation at first; but on cooling, the lead salts of the solid acids precipitate in a crystalline form, which can be filtered with great rapidity and ease. This simple method of direct precipitation of solid fatty acids was long ago employed by Jean to separate a portion of the liquid acids and to obtain their iodine value in the examination of lard. It does not seem to be commonly used to separate and estimate the solid fatty acids. The present author, however, much prefers it to the well-known lead-salt-ether method, and has briefly referred to it in some previous publications.

Solubilities of Lead Palmitate and Myristate

The following experiments were made to test the accuracy of the results obtained by this method:

A solution of pure palmitic acid in hot 95 per cent alcohol was treated with an excess of lead acetate dissolved in hot alcohol. This precipitated on cooling and was allowed to cool further over night to a temperature of 16.5°C. It was then filtered and washed with 95 per cent alcohol. From the precipitate 98.8 per cent of the palmitic acid was recovered.

One hundred cc. of the filtrate, on decomposing with dilute nitric acid and collecting with ether, yielded 0.010 g. of palmitic acid; and 100 cc. of the washings, 0.004 g. of palmitic acid. This shows a sufficient insolubility of lead palmitate, for analytical purposes, in the filtrate, which contains lead acetate and acetic acid, and in the washings, which consist of 95 per cent alcohol.

The same experiment with pure myristic acid showed a solubility of lead myristate at 12°C., corresponding to 0.0175 g. of myristic acid in 100 cc. of the filtrate, and of 0.0110 g. in 100 cc. of the washings.

A slight impurity of the palmitic and myristic acid would have a considerable effect on the above results, so the solubility found in this way must be considered as a maximum.

The solubilities of lead laurate, eruceate, or iso-oleate have not been determined in this manner; but in most fats and oils palmitic acid would be the solid acid forming the most soluble lead salt, those of the higher saturated acids being less soluble.

Effect of Liquid Fatty Acids

As it seemed possible that the solubility of lead palmitate might be considerably increased by the presence in the solution of the liquid acids found in most fatty acid mixtures, and as the author knew of no way to prove directly the presence or absence of small quantities of solid fatty acids in the liquid acids of the filtrates, the following indirect method was used:

The fatty acids of cottonseed oil contain about 25 per cent of a solid acid, which is almost pure palmitic acid. A hot alcoholic solution of the cottonseed oil fatty acids was precipitated as above with lead acetate *insufficient* to combine with all the palmitic acid. On cooling to 22°, filtering, and adding to the filtrate a few drops of a dilute alcoholic solution of sulfuric acid, a mere trace of lead was found, while the filtrate obtained after cooling the liquid to 16° contained no lead that could be detected with alcoholic sulfuric acid, showing that, with palmitic acid in excess, lead palmitate is practically insoluble at 16° in 95 per cent alcohol containing liquid fatty acids, palmitic acid, and a small amount of acetic acid; and it seems probable that, with lead acetate in excess, the lead palmitate would be equally insoluble.

The same experiment was performed with fatty acids containing iso-oleic acid. Sufficient lead acetate was used to combine with all the stearic and palmitic acids, but not enough to combine with all the iso-oleic acid. At 13° the filtrate contained the merest trace of lead, showing that lead iso-oleate is practically insoluble under these conditions.

Though the liquid fatty acids can be separated fairly free from solid acids, it has hitherto been found impossible to obtain the solid acids free from liquid acids, either by the method herein described or by the old lead-salt-ether method. Lewkowitsch[1] states that the iodine value of the solid fatty acids obtained by the latter method will, as a rule, be in the neighborhood of 10, provided there is no erucic acid, etc., present, and he quotes a table of Tortelli and Fortini, in which the solid acids of cottonseed oil are given as having an iodine value of 19! If our object were only to determine the amount of solid acids in a mixture, a rough correction might be made for this iodine value; but it is generally very desirable to obtain the solid acids in a pure state so that, for instance, their neutralization value (mean combining weight) can be exactly determined, also their melting points, etc., and finally so that if they have an iodine value this shall indicate not an imperfect separation of liquid acids, but shall prove the presence of *unsaturated solid* fatty acids.

It has been found in using the method described in this paper that the solid acids separated from the lead salt precipitate will have an iodine value generally ranging from 3 to 10 per cent, and no amount of washing of the precipitate will lower this figure. Even ether, in which lead oleate, linolate, etc., are soluble, will wash practically nothing from the precipitate which has been exhausted with alcohol. Evidently there is formed a lead salt containing liquid fatty acid which is quite insoluble in alcohol containing acetic acid and in ether.

[1] Received June 22, 1921.

[1] "Chemical Technology and Analyses of Oils, Fats and Waxes," 5th Ed., 1, 552.

This residue of liquid acids can, however, be removed from the solid acids by dissolving the latter in alcohol and reprecipitating with lead acetate; or more simply by removing the washed first precipitate from the filter, dissolving in boiling alcohol containing about 0.5 per cent of acetic acid and allowing this to cool, and precipitating again. Two precipitations in all are generally sufficient to reduce the iodine value of the solid fatty acids to 1 per cent or under, a trifling figure.

Analytical Process in Detail

Weigh in a beaker as much of the fatty acid as is estimated to contain 1 to 1.5 g. of solid acids. In the case of a very liquid oil this amount will be about 10 g., while in the case of tallow it will be only 2 or 3 g. Dissolve in 95 per cent alcohol. Dissolve 1.5 g. of lead acetate in 95 per cent alcohol. The total alcohol for the two solutions should be about 100 cc. Heat both solutions to boiling and pour the lead acetate solution into the solution of fatty acid. Allow to cool slowly to room temperature, and then for several hours, preferably over night, to about 15°C. Filter and test the filtrate for lead with a few drops of an alcoholic solution of sulfuric acid. If there is no precipitate, showing that lead is not in excess, the analysis must be repeated, using less fatty acid or more lead acetate. Wash the precipitate with 95 per cent alcohol until a sample of the washings diluted with water remains clear. Transfer and wash the precipitate from the filter back into the beaker, using about 100 cc. of 95 per cent alcohol. Add 0.5 g. of acetic acid and heat to boiling. The precipitate will slowly dissolve. Allow to cool to room temperature and then to 15°C. as before. Filter and wash with 95 per cent alcohol as before. Transfer the precipitate by washing the filter paper with ether into the beaker. Add sufficient dilute nitric acid to decompose the lead salts. Pour and wash the whole mixture into a separatory funnel and shake. Wash with water until the washings are no longer acid to methyl orange. If a trace of nitric acid should remain with the ethereal solution it will act on the fatty acids in the subsequent drying. Transfer the ethereal solution to an evaporating dish, evaporate, dry, and weigh.

If desired larger quantities of material than those given above can easily be handled.

Results Obtained by Method

The figures of the following table are in accordance with the above directions. In each case two precipitations were made as described.

Sample Oils No.	Weight Fatty Acid Grams	Lead Acetate Grams	Alcohol for Each Precip. Cc.	Weight Solid Fatty Acids Grams	Per Cent	Iodine Value of Solid Fatty Acids
1. Cottonseed	5	1.5	100	1.1565	23.13	0.72
2. Soy bean	10	1.5	100	1.7010	17.01	0.85
3. Olive	10	1	100	1.0935	10.93	1.75
4. Peanut	20	3.5	300	[illegible]	16.78	0.80
5. Cottonseed	20	3	200	[illegible]	21.31	0.56
6. Lard	3	1.25	100	1.2005	40.02	0.58
7. Partly hydrogenated cottonseed	2.5	1.5	100	1.2655	50.62	42.21
8. Tallow	3	1.5	100	1.6085	53.62	4.38

The solid fatty acids of most of the fats and oils in this table have iodine values below 1 per cent.

Sample 7 is a partly hydrogenated cottonseed oil which would contain iso-oleic acid.[1] The iodine value of its solid fatty acids, 42.21, shows a large amount, $\frac{100 \times 42.21}{90} = 46.9$ per cent of an unsaturated solid fatty acid (iso-oleic acid). To confirm this figure, the solid acids were redissolved in alcohol and reprecipitated with lead acetate as before. The iodine value of the resulting solid acids was 40.07, only slightly below the value found above.

Sample 8 is a sample of beef tallow, the solid fatty acids of which have the comparatively high iodine value of 4.38. On redissolving these solid fatty acids in alcohol and reprecipitating, their iodine value was reduced only to 3.89. This would indicate the presence in tallow of a small amount of an unsaturated solid acid, of which, however, we have no other proof.

If in the above process insufficient lead acetate is used to precipitate all of the solid acids, the precipitation is fractional, and the solid saturated fatty acids of higher molecular weight come down first. In this case liquid acids are not carried down with the solid and a second precipitation is not required. For example:

Thirty g. of peanut-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 12°, yielded 1.6935 g. of solid acids having a mean combining weight of 317.

Thirty g. of olive-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 11°, yielded 1.3770 g. of solid acids having a mean combining weight of 266 and an iodine value of 0.79.

---

[1] Moore, J. Soc. Chem. Ind., 38, (1919), 320t

ORGANIZATION OF CHEMICAL SALESMEN

A movement to organize a national association of chemical salesmen was started at a recent meeting of sales representatives of every branch of the chemical industries held at the Chemists' Club. It was felt that there is a broad field for service for an organization composed of members of the sales and advertising staffs, manufacturer's sales agents and executive sales officers of companies in every branch of the chemical industry. It was the unanimous opinion of those present that such an organization should concern itself with the broad commercial problems whose solution would react to the benefit of the entire industry, and that the questions of prices or sales policies of individual companies should not be included. An Organization Committee was appointed, to arrange for a general meeting at the time of the Exposition. This committee was composed of the following: Fred E. Signer, chairman, Butterworth-Judson Corporation; William Haynes, secretary, Drug & Chemical Markets; C. F. Abbott, National Aniline & Chemical Co.;

The Technical Committee on Standardization of Petroleum Specifications held a meeting at the Bureau of Mines in Washington recently to consider a number of changes in the specifications used by the Government for the purchase of kerosene, gasoline, fuel and lubricating oils. Dr. N. A. C. Smith of the Bureau of Mines was chairman of the meeting, and Dr. T. G. Delbridge of the American Society for Testing Materials and the American Petroleum Institute represented the several engineering societies constituting the Advisory Board. It was decided to give further study to the new methods which have been approved by the American Society for Testing Materials before deciding upon their adoption. The methods include the following tests: corrosion, flash, distillation, sulfur, cloud and pour, saponification in place of fatty oil, water and sediment, precipitation, viscosity, and melting point.

Determination of Metallic Aluminium and of Aluminium Oxide in Commercial Metal[1, 2]

By Julian H. Capps
Bureau of Mines, Pittsburgh, Pennsylvania

One of the most vexatious problems confronting the aluminium industries is the question of determining the oxygen content of aluminium. Considerable evidence is at hand to indicate that this impurity may be present in surprisingly large amounts and that it may exert profound influences on the properties of the metal. But no really dependable and trustworthy method has been developed for its quantitative determination.

A number of methods are in use. Of these the method of Rhodin[3] has been more widely accepted than any other. This is based on the assumption that 10 per cent caustic soda solution dissolves metallic aluminium quantitatively without attacking the oxide which is present. The laboratories of a metallurgical company have proposed a method employing iodine as a reagent for the same kind of a selective attack, and another laboratory recommends 50:50 hydrochloric acid for the purpose. This last method may be modified by adding potassium chlorate.

These four methods were tried out on a large sample of small millings from an ingot of secondary No. 12 alloy (8 per cent copper). This metal was procured from melting down clean borings and was thought to contain a rather high percentage of aluminium oxide. Five-gram samples were exposed for different, specified lengths of time to the action of the reagents.

The results of these determinations, expressed as per cent oxide in terms of Al_2O_3 weighed, are shown in Table I. No agreement among methods is evident here. The length of time of exposure to the reagents appears to exert no definite influence.

Table I

Reagents	Time of Action			
	1 Hr.	24 Hrs.	7 Days	35 Days
NaOH	1.9	2.21	2.28	1.68
Iodine	0.09	0.05	0.05	0.06
HCl	0.36	0.15	0.41	None (no ppt.)
$HCl + KClO_3$	0.05	2.15 (?)	Impossible to filter	0.09

This alloy contained, according to separate analyses:

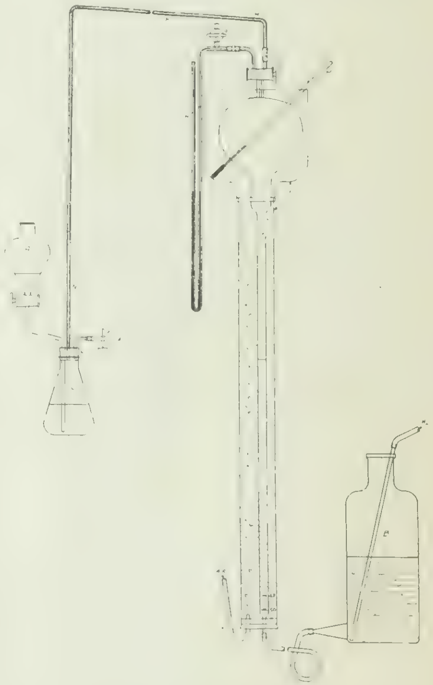
	Per cent
Fe	1.33
Si	0.59
Cu	8.06
Al_2O_3 plus Al	90.02 (By difference)

Another quite different method developed for the evaluation of aluminium powder[4] makes use of the reducing property of aluminium in a thermite reaction. Lead oxide is reduced by the sample at high temperature, under a flux of borax. Accuracy within 1 per cent is claimed for this method, but the present author has had no success in attempts to put it into practice.

A certain amount of evidence has been cited indicating the existence of an oxide or oxides of aluminium other than Al_2O_3. Rhodin[5] produces evidence of the existence of a compound Al_3O_4. M. Pionchon,[6] in 1893, concluded that aluminium, oxidized directly, produces a compound Al_2O. Duboin[7] believes this Al_2O to be a mixture of $4\,Al + Al_2O_3$. Kohn-Abrest[1] saw the effect of temperature on the degree of oxidation of aluminium powder and concluded that AlO was the final product.

It is possible, also, that elemental oxygen may be present, occluded or dissolved as such. The solubilities of gases in aluminium have not been determined. But for the purposes of this investigation, combined oxygen alone is considered. Because of the strong reducing power of aluminium, it is assumed that no oxide other than one of aluminium can be present.

After a long search for a new method of determining this oxide, the results of which will be published in detail in a later paper, an apparatus and procedure have been developed which at once permit of rapid, direct determination of aluminium (and of oxide, by difference) and avoid certain potential sources of error in the wet methods mentioned above.



The metal is taken into solution by a reagent, either caustic or acid, under such conditions that all of the hydrogen liberated by the reaction is caught in a measuring buret, where its volume, temperature, and pressure may be read accurately. This gas is equivalent in quantity to the unoxidized aluminium, together with whatever iron is present when an acid reagent is used, or with the silicon, when caustic is used. Whether or not oxide of aluminum goes into solution is immaterial. If this be Al_2O_3, no gas will result from its solution; if Al_3O_4, for example, it is thought that enough gas will be evolved in its dissolution to correspond with the passage of this "lower oxide" to a compound of the trivalent Al_2O_3.

---

[1] [illegible]

[2] [illegible] Bureau of Mines.

[3] [illegible]

[4] H. [illegible] THIS JOURNAL, 12 (1920), [illegible]

[5] [illegible]

[6] *Compt. rend.*, **117** (1893), 328.

[7] *Compt. rend.*, **132** (1901), 826.

[1] *Compt. rend.*, **141** (1905), 323.

APPARATUS

The apparatus, shown in Fig. 1, consists essentially of a reaction flask, C, connected to the measuring buret, E. Flask C is equipped with a 3-hole rubber stopper, L, which bears the dropping funnel, A, for the admission of the reagent solution, the outlet tube, G, whose use will be spoken of later, and the capillary tube, F, which leads the gas to E for the necessary measurements.

The buret, E, was made from ordinary laboratory equipment. A 750-cc. glass flask was used for the bulb. Its neck was sealed to the top of an accurate 50-cc. buret, such as is used in ordinary volumetric analytical work. To the base of the flask was sealed a 2-way stopcock to connect E with F and with the water manometer, H. Water was used as the confining liquid in E, and its level was controlled by the bottle, B. The water jacket, J, was made from a length of 2-in. glass tubing joined to the mouth of a large reagent bottle, from which the base had been cut. The water in this was kept stirred by a constant stream of air which bubbled up from K.

The first method of reading buret E was simply to raise B until the level of the water in it coincided with that in the buret. This, however, introduced an almost constant error due to capillarity in the latter. Hence the outfit was equipped with the water manometer, H. In a number of runs the buret was read by both these methods for comparison. It was found that from 0.1 to 0.2 cc. error in volume was made in each reading by the first method. The average error in twenty-three such comparisons was 0.16 cc., which correction was applied. All "old" results were recalculated to the basis of the "manometer" reading.

The calibration of the gas measuring device was accomplished as follows: Set up in its water jacket in the position shown in Fig. 1, with conditions exactly the same as those obtaining when in actual use, the gas container was carefully cleaned with strong caustic soda solution and with chromic acid, and rinsed thoroughly with tap water and with distilled water. It was then filled, including cock D, with distilled water saturated with air. After it had stood thus for a couple of hours and had come to the same temperature as the water in the jacket, it was allowed to run out to some point in the graduated portion, through a specially made tube fitted with a cock, into a tared flask, in which it was carefully weighed. After 15 min. (to allow for drainage from the bulb), the water level in the graduated part was read. The temperature of the water was known from that of the jacket.

The weight of water, divided by the density of air-saturated, distilled water, weighed in air against brass weights, gives the volume occupied at the known temperature. From this, the reading of the buret was subtracted, and the resulting volume represented that of the measuring flask to the first, or "zero" graduation.

Three calibrations made according to this procedure gave 778.74, 778.84, and 778.76 cc. The average, 778.78, is called 778.8 for actual use, since the buret can be read with accuracy to only about 0.05 cc.

In order to make unnecessary the careful reading of the barometer once or twice for each run, a compensator, such as is used in Orsat gas analysis equipments, was installed. It had a volume of about 100 cc., contained a little water, and was immersed in the water jacket along with E. It was satisfactory over periods when changes in the temperature of the jacket and in the atmospheric pressure were small, but not at all satisfactory otherwise. Its strange behavior could not be explained, and lest it prove misleading, it was discarded.

It was feared at first that the rather large solubility of hydrogen in water would introduce an error too large to be neglected, and attempts were made to eliminate this source of possible inaccuracy. A strong solution of potassium carbonate, in which hydrogen is soluble to a very limited extent, and the aqueous vapor pressure of which was plotted over a sufficient range of temperature, was tried as the confining liquid in E. This seemed successful enough, but its use was abandoned because its advantages did not compensate for its disadvantages. Distilled water was found to be the best confining liquid, and, when it was kept saturated with hydrogen by a continuous stream of bubbles in B, no loss from solution of the gas under investigation could well take place. Hydrogen has often been kept over water in E over periods of several days duration without suffering any measurable loss.

PROCEDURE

A sample of the aluminium under investigation is weighed into the Erlenmeyer flask, C, with an accuracy of 0.1 mg., and a little distilled water is introduced and brought to a boil over a burner. This drives out what gases may be dissolved in the water and serves to rid the metal sample of air that may be adsorbed thereon. As soon as this has boiled for a few seconds, the flask is almost filled with cold, distilled water (previously boiled to expel all air), its neck is moistened, and it is connected firmly to the stopper, L. Tube G is open. Now, by raising B, E is filled completely with water to a point, M, in the capillary tube. Cock D is now closed. Flask C is filled completely with water from A until its level reaches the stopper, L, and water runs out through G. G is now closed, and preparations for the determination are complete.

A quantity of reagent is admitted to A and allowed to run into C, displacing an equivalent volume of water through G. When gas evolution commences, G is closed, and the increasing volume of gas collecting in C forces solution back into A. This displacement may be accelerated by heating C. A very small amount of gas may be carried out of C suspended in the reagent liquid. But when the operation is carefully performed, it does not amount to enough to introduce any sensible error. When about half the liquid is displaced from C into A, the "free space" formed is deemed sufficient for more rapid gas evolution. So the cock of A is closed, and D is opened. A fresh supply of new reagent is now admitted and the gas evolution may become violent. As this action slows up, C is kept heated by a burner until all action is complete, when, by admitting more liquid from A, all the gas is forced over into E. The liquid of C now stands in F to about the point N. The small capillary, F, is gas filled after the reaction as well as before, so no appreciable error is introduced here.

Cock O is opened, if necessary, to equalize water levels in the manometer, H. With O closed, cock D is next turned to connect E with H, and the water levels of H are again equalized by adjusting the height of B. Now the pressure upon the confined gas in E is identical with the atmospheric pressure of the room.

The level of the confining water in the graduated part of

E is carefully read and recorded, as are also the temperature of the water jacket and the barometric pressure.

After 10 or 15 min. these same adjustments and readings are repeated. By this time drainage of water from the walls of E will have been more thorough, the gas will more certainly have attained the temperature of the jacket, and any supersaturation of it by water vapor will have become relieved by condensation.

Temperature (t) is read to 0.1° C., pressure (p) is read to 0.1 mm. of Hg, and volume (v) is read to 0.05 cc. The gas is calculated to standard pressure and temperature by applying the formula

$$v \times \frac{p - \text{vapor pressure of water at } t}{760} \times \frac{273}{273+t} = V.$$

Calculations were made by the use of a table of five-place logarithms.

Probable Error

The accuracy of these gas measurements may be judged by the following:

Error in Reading	Resulting Error of Gas Volume (S.T.P.) Cc.	Resulting Error of "Per cent Al" Per Cent
0.1 mm. in barometer	0.1	0.014
0.1° C. in thermometer	0.21	0.034
0.1 cc. in buret	0.1	0.01
Totals	0.44	0.058

This shows the inherent error of the measurement. Other errors may be introduced from other causes unless care is exercised.

If hydrochloric acid is used to act on the aluminium, an amount of HCl may be carried into E with the hydrogen. This would dissolve in the film of water adhering to the walls of E, lower the aqueous vapor pressure of this film, and cause an inaccurate, low reading of gas volume. By the proper choice of reagents, this source of error can be avoided.

As previously stated, the solubilities of gases in aluminium are not known, but some idea of the gas content of the metal is furnished by Gwyer,[1] who found that cast aluminium which showed exceptionally severe blistering after rolling into sheet and annealing contained one-tenth to one-third of its own volume of occluded gas, that the composition of the gas varied exceedingly, and that its chief constituent was hydrogen.

This severe blistering is the result of unusually large amounts of gas being occluded; more gas, that is, than should be looked for in ordinary primary metal such as the sample used in this investigation. However, if the worst conditions which Gwyer cites should obtain in this sample (gas to the extent of one-third the volume of the metal), they would introduce an error too small to alter the results materially.

Thus, the density of Al is about 2.7 and the sample employed in this work is about 0.564 g. Hence the volume of Al used was only 0.21 cc. One-third of this, or 0.07 cc., is of the order of magnitude of the probable error of reading the buret, and could throw the result of a determination in error by less than 0.01 per cent of the sample weight.

The fact that hydrogen is the chief gaseous impurity in aluminium is confirmed by other investigators, notably Guichard and Jourdain[2] and Dumas,[3] though Sieverts[4] states that aluminium does not dissolve hydrogen.

Theoretical

The weight of a liter of dry, pure hydrogen at 760 mm. pressure and 0° C. temperature is taken as 0.08994 g. (the value accepted by the U. S. Bureau of Mines). From this, it follows that 1 g. of "100 per cent pure" aluminium should displace 1.24068 liters of hydrogen (27.1 being the atomic weight of aluminium).

If an acid is used as the reagent, the reaction

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

will take place along with the reaction

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4) + 3H_2$$

So the hydrogen collected will represent the iron present, as well as the metallic aluminium. If caustic soda is used, it interacts with silicon according to the reaction

$$4NaOH + Si \longrightarrow Na_2SiO_4 + 2H_2$$

In this case, of course, the H_2 represents Si and Al. The amounts of these impurities must be known from separate analyses of the metal. However, these are the substances which are always determined in ordinary analyses of aluminium and, with copper, which is not acted on by either alkalies or nonoxidizing acids, are the chief impurities present.

1 g. Fe liberates 401.34 cc. H_2 (S.T.P.)
1 g. Si liberates 1584.09 cc. H_2

Hydrogen equivalent to the iron present or to the silicon, depending upon the nature of the reagent, is subtracted from V, the total hydrogen reduced to 0° C. and 760 mm. This corrected volume, divided by 1240.7, gives the weight in g. of metallic Al represented, the ratio of which to the weight of the original sample yields per cent metallic Al.

All other constituents (Cu, Fe, Si, and, if necessary, Zn, Mn and Mg) in the sample are known from separate analysis. The difference between the sum of all these plus metallic aluminium and the total weight of the sample is taken as aluminium oxide. This value may represent actual Al_2O_3 or a larger amount of Al in a lower state of oxidation.

CARBIDE AND NITRIDE—The probable presence of aluminium nitride and carbide is not overlooked, although these have not been considered in this work for the reason that the extent of the contamination of the metal used by these substances is very slight.

The attack of the reagent upon the sample would affect these impurities according to the following reactions:

$$4AlN + 6H_2O = 4NH_3 + 2Al_2O_3 \qquad (1)$$

$$Al_4C_3 + 6H_2O = 3CH_4 + 2Al_2O_3 \qquad (2)$$

From the former, ammonia would be formed, which, if it passed into the gas measurer, would be readily dissolved in the water, and so would not affect the volume of the hydrogen, unless its amount were too large to be completely dissolved or to leave the aqueous vapor pressure of the water film unaltered. In other words, no gas would be measured from the nitride and this substance would be represented as part of the oxide present.

Reaction 2 shows that carbide will produce methane, which will pass into the measurer and be treated as hydrogen. The amount of aluminium which is in this carbide would, if metallic, produce hydrogen to the extent of just twice the volume of this methane.

Now, since the aluminium in aluminium carbide is roughly seven-tenths of the weight of the carbide, it follows that the error introduced by a given percentage of carbide will be in increasng the apparent percentage of metallic aluminium, and by an amount equal to about one-third of the percentage of carbide in the sample.

Thus, if 3 per cent carbide be present, and gives off, say, 20 cc. of CH_4 (which will be measured as hydrogen with which it is mixed), the same percentage (3) of metallic aluminium would give 60 cc. So the effect of the carbide will be to increase the apparent metallic aluminium content. The amounts of carbide occurring in commercial metal are so small, however, that this factor may safely be neglected.

---

[1] In the discussion of papers on "Occlusion of Gases by Metals," *Trans Faraday Soc.*, 14 (1920), 2[illegible]

[2] *Compt. rend.*, 155 (1912), 160.

[3] *Compt. rend.*, 90 (1880), 1027.

[4] *Elektrochem.*, 16 (1910), 707.

DATA

The performance of this apparatus was tried out on a sample of primary aluminium millings from a piece of ingot sent by Mr. J. G. A. Rhodin of H. L. Raphael's Refinery, London, England.

Analysis of this material, made by Mr. Rhodin, showed the following composition:

	Per Cent.
Al	98.60
Al_2O_3	0.52 (Rhodin's method)
Fe	0.38
Mn	0.01
Pb	0.02
Cu	0.07
Sn	0.03
Si	0.44
	100.07

Betwen 0.56 and 0.57 g. of this metal were found to furnish enough hydrogen under the conditions of the experiment to fill the measuring device about midway in the graduated section.

A great many runs were made, and some strangely variable results were obtained before it became evident that the treatment of the sample before a determination is an important consideration. Surfaces adsorb quantities of gases. Failure to take this fact into account, or the wrong assumption that such gases are present in or on these millings in amounts too small to introduce an important error, has vitiated a large amount of otherwise good data.

WITH SODIUM HYDROXIDE—The series of results in Table II shows the effect of this adsorbed gas.

The procedure here was to cover the aluminium sample, in its Erlenmeyer flask, with about an inch of cold, air-free (previously boiled), distilled water, and to warm this or boil it over a Bunsen burner as specified below. After a sample had boiled as long as desired, it was immediately chilled by filling the flask with more cold water. Next, the flask was connected in the position of C, shown in Fig. 1, and the determination made as already outlined, caustic soda being used as the reagent.

The average sample, about 0.564 g., contains, according to the analysis, 0.0025 g. Si, which produces 3.93 cc. of hydrogen when oxidized by caustic soda. This volume was subtracted from the total volume of hydrogen produced in each run and the remainder divided by 1241. This result, divided by the weight of the sample, gives the figure (Column 1), which is called "per cent Al."

TABLE II—SODIUM HYDROXIDE AS REAGENT

Run	Sample Wt. Grams	Vol. of H_2 at S.T.P. Cc	I Per cent Al (1241 Value)	Previous Treatment	II Recalculated (1254.1 Value)
104	0.5623	700.85	99.87	Not heated (cold water)	98.83
105	0.5650	704.15	99.86	90 (small amt. of gas)	98.82
106	0.5652	702.83	99.64	90 (vacuum boiled)	98.60
107	0.5672	705.73	99 70	*Almost* boiled	98.66
108	0.5637	701.13	99.665	Boiled hard 5 sec.	98.63
109	0.5638	701.23	99.66	Boiled hard 15 sec.	98.62
110	0.5666	704.47	99.63	Boiled hard 15 sec.	98.59
111	0.5631	700.15	99.63	Boiled hard 30 sec.	98 59
112	0.5620	698.50	99.59	Boiled hard 1 min.	98.55
113	0.5665	704.49	99.65	Boiled hard 3 min.	98.61
114	0.5621	699.10	99.66	Boiled hard 3 min.	98.62
115	0.5667	704.85	99.67	Boiled hard 15 min.	98.63
116	0.5642	701.57	99.64	Boiled hard 15 min.	98.60
117	0.5650	702.28	99.60	Boiled hard 60 min.	98 56

Numbers 104 and 105 show much higher results than the rest, because the total gas volumes in these runs represent what gas was adsorbed on the sample as well as the hydrogen from the reaction. The average of Runs 108 to 117, inclusive, is close to 99.64 per cent, which is about 0.23 per cent lower than 104 and 105. Thus it would seem that enough adsorbed gas was present in these two to make an error of 0.23 per cent in a determination. From this it appears that 1 g. of these coarse aluminium millings holds in the neighborhood of 2.9 cc. of gas (air and CO_2) adsorbed.

This is borne out by the chemical analysis of the hydrogen taken from a run in which the sample had not been boiled before treatment. Analysis was made in the gas laboratory of the Pittsburgh Station, Bureau of Mines.

	Per Cent.
CO_2	0 16
O_2	0 07
N_2	0.47 (Difference)
H_2	99 3

Total gases other than hydrogen constitute 0.7 per cent of the whole. According to the above figure for adsorbed gas, this sample held 1.65 cc. The volume of the connecting tube, F, which was filled with air before the run, is about 1.5 cc. This total, 3.15, accounts for about 0.45 of the 0.70 per cent impurities. The remaining 0.25 per cent is within the accuracy of the Orsat combustion method, by which the hydrogen was determined in the above gas analysis.

Runs 108 through 117 are taken as indicating the true value of the hydrogen from the main reaction. Their relative constancy over a range of from 5 sec. to 1 hr. of boiling would indicate that no appreciable chemical attack is made upon the metal by boiling water.

Run 106, in which the water was not heated higher than 90°, and in which violent boiling was induced by reducing the air pressure, shows that the simple driving off of gaseous impurities from the metal surface is all that takes place when the sample is treated with boiling water.

The value of 99.64 per cent Al is 1 per cent higher than the actual content as determined directly by Rhodin. Since there is little room for doubt about the volume of the apparatus and about the analysis of the sample, the reason for this discrepancy must be that the wrong value has been used for the volume of hydrogen which will be set free by a unit weight of aluminium.

Calculating back from 99.64 to a basis of 98.60 per cent, it appears that 1 g. of pure aluminium produces 1254.1 cc. of hydrogen, measured at 0° C. and 760 mm. This would indicate 26.81 as the atomic weight of aluminium, a value more than 1 per cent lower than the present accepted value of 27.1. This is as much lower again as is the value (26.963) obtained by Richards and Krepelka,[1] in the latest work on the atomic weight of this element.

Of earlier investigators, Mallet,[2] Thomsen,[3] and Kohn-Abrest[4] used measurements of hydrogen resulting from solution of analyzed aluminium for determining the atomic weight, and all found values close to 27.0. However, none of them took account of the presence of any oxide of aluminium in the samples used. Al was known only by difference. If oxide had really been present in the metal, their results would be too high.

Nicolardot and Robert[5] obtained a value of 1242.89 cc. per g. as the volume given from the reaction of sodium hydroxide on a sample of aluminium of known composition and calculated to a basis of 100 per cent pure metal.

Nicolardot[6] has described an apparatus, somewhat more complicated than the one described herein, by which he suggests that aluminium and other metals may be investigated an deven that atomic weights may be determined.

---

[1] *J. Am. Chem. Soc.*, **42** (1920), 2221
[2] *Phil. Trans.*, **181** (1880), 1003.
[3] *Z. anorg. Chem.*, **15** (1897), 447.
[4] *Bull. soc. chim.* [3], **33** (1905), 121.
[5] *Chimie & industrie* **2** (1919), 641
[6] *Bull. soc. chim.* [4], **11** (1912), 406.

Adopting the figure of 1254.1 cc. as the volume of hydrogen given off by the action of 1 g. of pure aluminium on a reagent, and recalculating the data already shown to this basis, the values in Column II, Table II, are obtained. These are in accord with the careful analysis of Rhodin.

WITH SULFURIC ACID—A series of runs was made with sulfuric acid, which are tabulated in Table III. To the author's surprise, it was found from the hydrogen figures, and also from tests of the filtered reagent solution after the runs, that the acid had dissolved not only the iron, but also the silicon present, oxidizing it to silicic acid. So this "total hydrogen" had to be corrected for the gas from both the iron and the silicon.

Strange to say, these figures vary pretty widely, by 0.5 per cent, but their average is close to that of the runs made with caustic soda. The acid is slow to act on aluminium, and a strong solution must be employed and the temperature kept near boiling by a burner. Even under these conditions a determination is a matter of several hours.

TABLE III—SULFURIC ACID AS REAGENT
(Sample boiled 30 sec. in every case)

RUN	Sample Wt. grams	Vol. of H_2 at S.T.P. Cc.	Per cent Al (Corrected for Fe and Si) Basis, 1254. 1Value
137	0.5712	711.20	98.60
138	0.5710	712.60	98.83
139	0.5639	700.27	98.35
140	0.5663	706.18	98.76
141	0.5638	702.70	98.70
142	0.5637	701.67	98.58
143	0.5634	703.25	98.85
144	0.5658	702.73	98.36
145	0.5681	708.13	98.72
		AVERAGE	98.64

PRECAUTIONS

This method is by no means "fool proof," but, when operated intelligently and with proper attention to details of manipulation, determinations can be run off at the rate of about two per hour.

Care must be taken to bring the water over the sample to violent boiling before making a determination. This drives off occluded air from the surfaces of the metal particles. It is best to let this boiling continue for perhaps half a minute.

All water used in filling the reaction flask must be boiled before use to free it from all dissolved air.

Close attention must be given during the early stages of a run to prevent any small metal particles from being carried by the reagent solution out of the reaction flask and into the dropping funnel, where its equivalent of hydrogen would be lost to the determination.

The reaction flask must be completely filled with pure water to the exclusion of all air bubbles before the admission of any reagent.

The gas measuring apparatus must be cleaned as often as necessary with strong caustic solution or chromic acid, or both. Otherwise, grease from the stopcock, which is carried into the apparatus, prevents proper drainage of water from the surfaces and interferes with the reading of the meniscus. For such cleaning, the outfit need not be taken apart. A tube may be attached to the lower end of the buret, and through this the cleaning solutions, wash waters, etc., may be taken into the apparatus by suction.

The rubber stopper, L, should be fitted carefully to the reaction flask and tested frequently, lest small leaks develop which would admit air into the flask. When hydrogen is passing into the gas measurer the pressure in the reaction flask is less than atmospheric, so during this time leaks would be inward.

ADVANTAGES OF THIS METHOD

This method and apparatus have the following advantages over other methods which have been used or suggested:

1—RELATIVE SIMPLICITY OF APPARATUS AND MANIPULATION—The entire equipment is assembled from ordinary laboratory glassware and a good glassblower can make the necessary alterations in a couple of hours. When the exercise of proper care in handling becomes habitual, the use of this apparatus is simple and easy.

2—RAPIDITY OF ANALYSIS—When a very active reagent is used, *i. e.*, caustic soda, runs may be made at the rate of about 30 or 40 min. each. With less active reagents, the process is slower.

3—REPRODUCIBILITY OF RESULTS—When metal, reagent, and other factors are kept the same, results will be found to check one another surprisingly closely. The author has made series of runs on a sample of primary metal, with hydrochloric acid, in which as many as ten or twelve consecutive determinations agreed within 0.06 per cent of the total sample weight, which is the probable error of the measurement (see page —). Lack of homogeneity in the metal sample is the most potent cause of wider variations in results.

4—Only one weighing is necessary for a determination. Calculations made with logarithm tables require no more than about 5 min.

5.—The method is applicable over a wide range of metal composition.

DISADVANTAGES

The disadvantages of the method are as follows:

1—It is realized that the accuracy of this method is not subject to rigorous proof. No aluminium of very high purity, known to be free from oxide, is obtainable with which to test it. Also, knowledge of the exact oxide content of the metal at hand and of the composition of such oxide within the metal, is not available further than is shown by Rhodin's own analysis of the metal used, by his own method, a method which is itself based upon assumptions that have never been proved, and for which great accuracy and dependability are not claimed.

2—On account of the peculiar conditions of procedure, this method is not applicable to metal in a fine state of subdivision. The particles should be no smaller than will be retained by a 30-mesh screen; otherwise they are easily carried out of the reaction flask suspended in the reagent solution. Coarse drillings, millings, and turnings are best adapted. The only types of aluminium with which this method could not be used, however, are bronze powder, dust, and grindings. Pig metal, castings, sheet metal and so on, which comprise the vast bulk of the metal of commerce, furnish coarse borings and turnings with ease. So this limitation does not amount to a serious circumscription.

CONCLUSION

Accurate estimation of metallic aluminium (and of oxide, indirectly) in commercial metal may be made by measuring the hydrogen evolved from reaction between it and a reagent.

By the method herein set forth these values can be determined rapidly and easily. There has long been a really great need of such a method, because aluminium is now bought on pecifications based on a "difference" method of analysis, which utterly fails to consider oxide, nitride, carbide, and possibly other impurities which are undoubtedly almost always present. The ordinary analysis calls for determination of copper, iron, and silicon, and the difference is said to be aluminium. As a matter of fact, this ordinary incomplete analysis is inadequate, giving only a superficial idea of metal quality. The present method supplies a long-felt need.

ACKNOWLEDGMENT

The author wishes to acknowledge his debt to Mr. Robert J. Anderson, of the Bureau of Mines, for very valuable assistance and suggestions, and to Mr. John G. A. Rhodin, of H. L. Raphael's Refinery, London, England, for analyzed aluminium samples.

A Rapid Method for the Determination of Sodium Chloride in Soap[1]

By H. C. Bennett

Los Angeles Soap Company, Los Angeles, California

The usual method for the determination of sodium chloride in soap calls for the decomposition of the soap by sulfuric acid, and the volumetric estimation of the sodium chloride by titration with 0.1N silver nitrate, using potassium chromate as an indicator.[2]

When one is called upon to analyze soaps containing a large amount of silicate of soda or insoluble fillers such as silica or talc, this method proves to be somewhat difficult of manipulation. The method described below, however, is not open to this objection and is quick and accurate. For this reason also it is valuable in routine control analyses in soap works laboratories. A complete determination can be easily made in 7 min.

The method depends upon the precipitation of the soap and admixed soluble fillers in a water solution by the addition of magnesium nitrate. The sodium chloride may then be titrated immediately with silver nitrate solution without filtering off the precipitated magnesium soap and other insoluble compounds. The indicator used is potassium chromate.

Magnesium nitrate was selected as the best precipitating agent to use because of the fact that it does not form an insoluble product with the potassium chromate, which is later used as an indicator in the titration. Solubility tables[3] show that magnesium chromate is very soluble in either hot or cold water, whereas calcium chromate is only moderately soluble in cold water, and much less so in hot water. Barium and strontium chromates are insoluble.

The method, in detail, consists of dissolving 5.85 g. of soap in 150 cc. of hot water in a beaker, boiling if necessary to effect solution of all soluble components. The soap and soluble fillers are precipitated out of solution by the addition of 25 cc. of a 20 per cent solution of magnesium nitrate (crystals). Without cooling, the unfiltered mixture is then titrated against 0.1*N* silver nitrate solution, using a small amount of potassium chromate as an indicator. The appearance of a reddish brown color is the end-point, and the percentage of sodium chloride is read directly from the buret by dividing the number of cubic centimeters by ten (1 cc. = 0.1 per cent).

Results by this method have been checked in this laboratory time after time against the usual standard method and have always agreed to within 0.01 or 0.02 per cent. Cooling the mixture before titrating increases the accuracy of the method. Soaps to which known amounts of sodium chloride were added have also been made in the laboratory, and the analysis by this method gave concordant results.

The author is indebted to Mr. E. L. Northrup, who performed the laboratory work necessary to demonstrate the feasibility of the method.

The Application of the Immersion Refractometer to the Analysis of Aqueus Salt Solutions[1]

By C. A. Clemens

South Dakota State Food and Drug Laboratories, Vermillion, South Dakota

In the past the immersion refractometer has been little used in the quantitative analysis of inorganic salt solutions, and then largely with solutions containing but a single salt. This fact may be explained by the lack and unreliability of data on refractive indices. Practically all data upon aqueous salt solutions prepared for quantitative work have been worked out and compiled by Wagner.[5] They take the form of tables worked out for definite temperatures, necessitating the accurate control of temperature, which is a serious drawback in ordinary analytical work.

In this paper it is proposed to demonstrate that the immersion refractometer furnishes a very rapid and, at the same time, fairly accurate method for the determination of soluble salts in aqueous solution, both singly and in simple mixtures; and, furthermore, that the use of tables can be avoided by the determination of a constant for each salt, which constant is applicable at ordinary room temperatures.

THE REFRACTIVE INDEX FACTOR

Jones and Getman[6] measured the refractive indices of several solutions, and in every case they found the refractive index to be a linear function of the concentration. Hallwachs[7] and Bender[8] obtained practically a constant value for

$$\frac{n - n_o}{c}$$

where n = refractive index of solution

n_o = refractive index of water at the same temperature

c = grams solute per 100 cc. solution.

From the above it is obvious that the value of one division of the immersion refractometer scale expressed in per cent by volume (g. in 100 cc. of solution) is equivalent to the reciprocal of $n - n_o/c$, the values of n and n_o being expressed in terms of the immersion refractometer scale, and that this value is a constant. It should be noted that when p (g. solute per 100 g. solution) is substituted for c, the values obtained increase with increased concentration. Robertson[1] has worked out such a constant for caseinates, while Zwick[2] and Lalin[3] established factors for tannins and starch, respectively. Robertson finds that "the difference between refractive index of the solution and that of water at the same temperature remains appreciably constant." Salt solutions were tested at different temperatures, and it was found that the above statement held true for them as well as for caseinates.

Cheveneau[4] has shown that ionization has no sensible influence on refractive index; Rimbach and Wintgen,[5] that complexes have no measurable effect, while Jones and

---

[1] Received June 8, 1921.

[2] THIS JOURNAL, 11 (1919), 785.

Van Nostrand's "Chemical Annual," 4th Ed.

Received April 2, 1921.

Über quantitative Bestimmungen wässeriger Lösungen mit dem Zeiss'schen Eintauchrefraktometer," Sonderhausen, 1907.

[6] *Am. Chem. J.*, 31 (1904), [illegible].

[7] *Wied. Ann.*, 47 (1892), 380.

[8] *Ibid.*, 39 (1890), 90.

[1] *J. Phys. Chem.*, [illegible] (1909), [illegible].

[2] *Chem. Ztg.*, 32 (1908), [illegible].

[3] *Z. ges. Brauw.*, 32 (1910), 231.

[4] *Z. physik. Chem.*, 74 (1910), 233.

[5] Compt. rend., 150 (1910), 866.

TABLE I.—THE EFFECT OF TEMPERATURE CHANGE UPON $N-N_0$

Formula of Salt	Per cent of Salt	$n-n_0$ Expressed in Immersion Refractometer Scale Divisions 18°C.	20°C.	23°C.	25°C.
NaCl	0.68	3.00	3.04	3.02	3.07
	6.66	29.75	29.68	29.65	29.62
$K_2Cr_2O_7$	2.01	9.38	9.35	9.38	9.39
	10.00	46.70	46.70	46.70	46.67
$Na_2S_2O_3$	1.79	9.37	9.43	9.37	9.31
	11.54	59.98	60.82	60.35	60.45
$MnCl_2$	1.51	8.47	8.39	8.35	8.51
	6.71	37.51	37.50	37.45	37.52
$KClO_3$	1.05	2.20	2.15	2.19	2.18
	5.13	10.69	10.72	10.70	10.68
$AgNO_3$	5.19	14.05	14.07	14.03	14.00
	10.45	28.26	28.21	28.19	28.17
$CaCl_2$	2.23	12.89	12.90	12.93	12.89
	7.06	40.80	40.81	40.79	40.82

Getman[1] find no effect due to hydration. The analytical data which follow later in the present paper tend to confirm the above work.

The foregoing establishes the fact that $c/n - n_o$ is, for all practical purposes, a constant independent of temperature and unaffected by dissociation, hydration, and the formation of complexes. This constant represents the per cent by volume of salt equivalent to one division of the immersion refractometer scale. Several of these constants have been worked out and are shown in the following table:

TABLE II.—REFRACTIVE INDEX FACTORS

NaCl	0.224	$AgNO_3$	0.370
K_2CrO_4	0.183	KNO_3	0.422
KI	0.298	$BaCl_2$	0.264
$Na_2S_2O_3$	0.191	$CaCl_2$	0.173
$MnCl_2$	0.179	$Cu(C_2H_3O_2)_2$	0.264
$K_2Cr_2O_7$	0.214	$HgCl_2$	0.448
NH_4NaHPO_4	0.206	$K_4Fe(CN)_6$	0.191
$KClO_3$	0.479	K_2SO_4	0.321
$MgSO_4$	0.186	$(NH_4)_2C_2O_4$	0.201
$Zn(C_2H_3O_2)_2$	0.242		

TABLE III.—DETERMINATION OF A SINGLE SALT IN AQUEOUS SOLUTION BY THE IMMERSION REFRACTOMETER

Formula of Salt	Refractive Index Water	Solution	Per cent. of Salt Present	Found	Difference
NaCl	14.70	17.70	0.68	0.68	0.00
K_2CrO_4	13.98	27.73	2.50	2.52	+0.02
KI	14.20	18.60	1.33	1.31	—0.02
$Na_2S_2O_3$	14.50	50.21	6.84	6.82	—0.02
$MnCl_2$	13.98	51.00	6.71	6.63	—0.08
$K_2Cr_2O_7$	14.10	37.57	5.05	5.02	—0.03
NH_4NaHPO_4	14.34	46.43	6.69	6.67	—0.02
$KClO_3$	13.81	18.11	2.06	2.06	0.00
$Zn(C_2H_3O_2)_2$	14.20	33.30	4.59	4.62	+0.03
$AgNO_3$	14.15	42.41	10.45	10.46	+0.01
KNO_3	14.08	30.60	7.06	6.97	—0.09
$BaCl_2$	14.32	22.61	2.17	2.19	+0.02
$CaCl_2$	14.30	44.25	5.21	5.18	—0.03
$Cu(C_2H_3O_2)_2$	14.21	25.71	3.01	3.04	+0.03
$HgCl_2$	14.13	25.39	5.00	5.04	+0.04
$K_4Fe(CN)_6$	14.33	64.48	9.61	9.58	—0.03
K_2SO_4	14.33	23.95	3.07	3.09	+0.02
$(NH_4)_2C_2O_4$	14.46	30.94	3.34	3.31	—0.03

APPLICATION OF METHOD

SINGLE SALT—The concentration of all solutions used in the following work is expressed as per cent by volume (g. solute per 100 cc. solution). All solutions were made up at 20°C. No temperatures were read while taking the refractive indices; instead, controls of distilled water were kept in the bath at the same temperatures as the solutions. Unless otherwise stated, refractive index refers to the immersion refractometer reading. In all calculations the anhydrous form of the salt was used. It is assumed that the salts are known qualitatively in every case.

Tables may be conveniently used in the methods described in this paper. If the table is prepared for temperature t and it is desired to work at temperature t', the readings may be corrected by subtracting the refractive index of water at t' from the refractive index of the solution at t' and adding the refractive index of water at t, thus obtaining the reading of the solution at the temperature t.

MIXTURES OF TWO SALTS, ONE OF KNOWN AND ONE OF UNKNOWN CONCENTRATION—The percentage of the salt of known concentration divided by its refractive index factor gives in terms of scale divisions the effect on the refractive index due to that salt. When this value is subtracted from the refractive index of the solution containing the two salts, the remainder is equivalent to the refractive index of the salt of unknown concentration in aqueous solution, and the percentage of salt present is determined in the manner explained before. Table IV gives illustrations of this application.

MIXTURE OF TWO SALTS, BOTH OF UNKNOWN CONCENTRATION—The procedure in this case is based upon that used by Leach and Lythgoe[1] in determining methanol in the presence of ethyl alcohol. This involves the use of the specific gravity or density of the solutions, and again we find a great lack of reliable data. However, it was found that a factor similar to the refractive index factor could be worked out. The specific gravities at 20°C./4°C. of various solutions were taken, and the value for water (0.99823) was subtracted. The values thus obtained were then divided by the respective percentages (by volume) of salt in the solutions. This gave the effect of the addition of 1 per cent of salt upon the density of the solution at 20°C. Table V gives several of these constants.

TABLE V.—DENSITY FACTORS FOR 20°C.

NaCl	0.00700	$AgNO_3$	0.00820
K_2CrO_4	0.00782	KNO_3	0.00602
KI	0.00718	$BaCl_2$	0.00866
$Na_2S_2O_3$	0.00791	$CaCl_2$	0.00753
$MnCl_2$	0.00821	$Cu(C_2H_3O_2)_2$	0.00585
$K_2Cr_2O_7$	0.00675	$HgCl_2$	0.00817
NH_4NaHPO_4	0.00773	$K_4Fe(CN)_6$	0.00652
$KClO_3$	0.00613	K_2SO_4	0.00778
$MgSO_4$	0.01055	$(NH_4)_2C_2O_4$	0.00470
$Zn(C_2H_3O_2)_2$	0.00655		

TABLE IV.—DETERMINATION OF ONE SALT IN A MIXTURE OF TWO SALTS BY MEANS OF THE IMMERSION REFRACTOMETER, THE SECOND SALT BEING DETERMINED BY OTHER MEANS

Refractive Index Water.	Mixture.	Diff.	Salt of Known Concentration Formula	Amount Present, Per cent	Calculated Effect on Ref. Index	Salt of Unknown Concentration Formula	Effect on Ref. Index Due to	Amount Present, Per cent	Amount Found, Per cent.	Diff.
13.48	60.70	47.22	NaCl	4.67	20.85	K_2CrO_4	26.37	5.00	4.83	—0.17
13.98	38.00	24.02	NaCl	2.33	10.40	K_2CrO_4	13.62	2.50	2.49	—0.01
14.23	28.83	14.60	NaCl	1.40	6.25	K_2CrO_4	8.35	1.50	1.53	+0.03
14.39	33.42	19.03	NaCl	1.17	5.22	K_2CrO_4	13.81	2.50	2.53	+0.03
14.39	39.29	24.90	NaCl	3.74	16.70	K_2CrO_4	8.20	1.50	1.50	0.00
13.91	32.84	18.93	$Na_2S_2O_3$	1.95	10.21	KI	8.72	2.77	2.60	—0.17
13.91	29.27	15.36	$Na_2S_2O_3$	0.99	5.18	KI	10.18	3.09	3.03	—0.06
13.91	39.18	25.27	$Na_2S_2O_3$	3.96	20.73	KI	4.54	1.27	1.35	+0.08
13.88	36.79	22.91	$MnCl_2$	3.35	18.72	KI	4.19	1.27	1.25	—0.02
14.00	29.30	14.70	$MnCl_2$	1.16	6.48	KI	8.22	2.58	2.45	—0.13
14.05	31.18	17.13	$Na_2S_2O_3$	2.04	10.68	$MgSO_4$	6.45	1.20	1.20	0.00
14.05	42.74	28.69	$Na_2S_2O_3$	1.02	5.34	$MgSO_4$	23.35	4.34	4.34	0.00
15.15	25.43	10.28	$AgNO_3$	2.61	7.05	KNO_3	3.23	1.28	1.36	+0.08
15.15	24.75	9.60	$AgNO_3$	1.35	3.65	KNO_3	5.95	2.50	2.51	+0.01
14.40	23.37	8.97	$(NH_4)_2C_2O_4$	0.73	3.64	K_2SO_4	5.33	1.70	1.71	—0.01
14.40	25.00	10.60	$(NH_4)_2C_2O_4$	1.67	8.31	K_2SO_4	2.29	0.77	0.74	—0.03

---

[1] *Loc. cit.*

[1] *J. Am. Chem. Soc.*, 27 (1905), 964.

The density of a solution at 20° C. can be calculated by means of these factors by multiplying the factor by the percentage of the salt and adding 0.99823. By reversing this process the percentage of salt can be found from the density.

Knowing the refractive index of the solution and of water at the same temperature and the specific gravity of the solution at 20° C./4° C., the percentage by volume of the two salts can be calculated as the following illustration shows:

Calculation of the Amount of Potassium Iodide and Sodium Thiosulfate in an Aqueous Mixture

Observed Data:

Specific gravity 20°/4° 1.02797
Immersion refractometer reading of mixture.........29.27
Immersion refractometer reading of water 13.91

The observed specific gravity minus the specific gravity of water,

$$1.02729 - 0.99823 = 0.02974,$$

divided by the respective specific gravity factors of the salts (Table V), gives the percentage concentration of single salt solutions having the same specific gravity as the mixture.

$$0.02974/0.00718 = 4.14 \text{ per cent. potassium iodide}$$
$$0.02974/0.00791 = 3.74 \text{ per cent sodium thiosulfate}$$

The per cent. of salt calculated from the specific gravity divided by the appropriate refractive index factor (Table II),

$$4.14/0.298 = 13.90$$
$$3.74/0.191 = 19.56$$

upon the addition of the observed reading for water, gives the refractive index readings of single salt solutions having the same specific gravity as the mixture.

$$13.90 + 13.91 = 27.81, \text{ refractometer reading for KI}$$
$$19.56 + 13.91 = 33.47, \text{ refractometer reading for } Na_2S_2O_3$$

The difference in refractometer readings of the respective salts,

$$33.47 - 27.81 = 5.66$$

divided into the difference between the observed refractometer reading and the reading for sodium thiosulfate alone,

$$33.47 - 29.27 = 4.20$$

gives the proportion of potassium iodide in the mixture taken as unity.

$$4.20/5.66 = 0.742 \text{ potassium iodide}$$
$$1.000 - 0.742 = 0.258 \text{ sodium thiosulfate}$$

Referring back to the possible content of each salt calculated from the specific gravity, and multiplying each by their respective proportional parts just found, we have:

$$4.14 \times 0.742 = 3.07 \text{ per cent potassium iodide}$$
$$3.74 \times 0.258 = 0.96 \text{ per cent sodium thiosulfate}$$

4.03 per cent total salts.

If the products of the refractive index and specific gravity factors lie close together, an error in the determination of refractive index or specific gravity causes a larger error in the final result than if they lie farther apart. The above method offers a rapid means of analyzing some mixtures which cause considerable difficulty when determined by ordinary analytical methods. Table VI gives a summary of a large number of determinations made by the above method. The range of concentration of the components is shown, as well as the maximum and minimum variation of the results from the truth.

Table VI

Combinations of Salts Used	Range of Concentration of Components Max. Per cent	Min. Per cent	Difference Between Concentration Found and that Known to be Present Max. Per cent.	Min. Per cent
$K_2CrO_4 + NaCl$	5.00	1.17	0.18	−0.01
$KI + Na_2S_2O_3$	3.96	0.99	0.21	−0.01
$NaCl + KI$	2.85	0.94	+0.08	−0.03
$K_2CrO_4 + Na_2S_2O_3$	5.00	0.99	+0.06	0.00
$MnCl_2 + KI$	3.35	1.16	+0.11	—0.04
$NaNH_4HPO_4 + Na_2S_2O_3$	2.36	0.99	+0.17	−0.01
$K_2CrO_4 + K_2Cr_2O_7$	5.00	1.00	−0.14	+0.07
$KClO_3 + K_2Cr_2O_7$	2.56	1.03	—0.04	+0.02
$MgSO_4 + Na_2S_2O_3$	4.34	1.02	—0.13	—0.04
$Zn(C_2H_3O_2)_2 + KClO_3$	1.75	0.65	+0.08	−0.02
$KNO_3 + AgNO_3$	2.61	1.28	+0.33	−0.21
$BaCl_2 + CaCl_2$	2.61	1.08	+0.06	—0.03
$Cu(C_2H_3O_2)_2 + HgCl_2$	2.50	1.00	+0.02	0.00
$K_4Fe(CN)_6 + K_2SO_4$	2.41	0.77	+0.06	−0.01
$(NH_4)_2C_2O_4 + K_2SO_4$	1.70	0.73	—0.04	0.00

MIXTURE OF THREE SALTS, ONE OF KNOWN CONCENTRATION AND TWO OF UNKNOWN CONCENTRATION—The method of calculation is best illustrated by an example.

Calculation of the Amount of Sodium Chloride and Magnesium Sulfate in the Presence of a Known Amount of Sodium Thiosulfate

Observed Data:

Specific gravity, 20°/4° 1.04366
Immersion refractometer reading of mixture........40.92
Immersion refractometer reading of water...........14.49
Concentration of sodium thiosulfate, per cent........ 2.04

The percentage of the salt of known concentration divided by its refractive index factor (Table II),

$$\frac{2.04}{0.191} = 10.68$$

gives in terms of scale divisions the effect on the refractive index due to the salt. This value subtracted from the observed refractive index,

$$40.92 - 10.68 = 30.24$$

yields a value equivalent to the reading of a solution containing only the two unknown salts in the same ratio and concentration as they occur in the above mixture.

The percentage of the salt of known concentration multiplied by its specific gravity factor (Table V),

$$2.04 \times 0.00791 = 0.01624$$

gives its effect upon the specific gravity. This value subtracted from the observed specific gravity,

$$1.04366 - 0.01624 = 1.02742$$

gives the gravity of the mixture as it would be provided the salt of known concentration were not present.

Using the calculated figures (refractive index, 30.24 and sp. gr. 1.02742), the percentage of the two salts of unknown concentration can be calculated in the manner illustrated for a mixture of two salts, both of unknown concentration.

The above method was employed by the author in analyzing the soluble portion of some "egg laying" tablets, which consisted of potassium chromate, sodium chloride, and magnesium sulfate. Another example of the application of this method was a stock tonic which consisted of sodium chloride, sodium thiosulfate, and magnesium sulfate. Table VII gives a summary of several determinations made by the above method. The range of concentration of the components is shown, as well as the maximum and minimum variation of the results from the truth.

Table VII

Combinations of Salts Used, the Quantity of the First Salt Named Being Known in Each Case	Range of Concentration of Components Max. Per cent	Min. Per cent	Difference Between Concentration Found and that Known to Be Present Max. Per cent	Min. Per cent
$Na_2S_2O_3 + NaCl + MgSO_4$	2.17	0.92	+0.14	+0.05
$Na_2S_2O_3 + NaCl + KI$	2.41	0.61	0.09	+0.02
$NaCl + MgSO_4 + K_2CrO_4$	2.30	1.15	—0.15	—0.11
$AgNO_3 + KNO_3 + KClO_3$	3.00	0.69	+0.14	+0.01
$MnCl_2 + BaCl_2 + CaCl_2$	2.49	1.04	+0.14	+0.04

The statement has been made earlier in this paper that the methods described are very rapid; consequently some statement of the time consumed by an analysis might be of value. A brief statement is given to show the average working time for the methods described in this paper, not including, however, time consumed by any volumetric or gravimetric determinations necessary to determine the concentration of the salt assumed to be known before the methods described are applicable. No account is taken of the time necessary to bring the solutions to constant temperature, as this requires little or no attention from the analyst. The estimation includes time consumed in calculation. In any case where only the refractive index is desired the time consumed should not exceed 10 min. When both the refractive index and specific gravity are to be determined, the time should not exceed 25 min. Both of these estimates are liberal, and the probabilities are that still less time than that stated would be sufficient.

Summary

Methods have been worked out for determining the per cent by volume (g. per 100 cc. of solution) of salts in aqueous solution by the aid of the immersion refractometer. The methods are applicable to single salts; mixtures of two salts, one of known and one of unknown concentration; mixtures of two salts, both of unknown concentration; mixtures of three salts, one of known and two of unknown concentration.

The per cent by volume of salt in aqueous solution necessary to cause a change of one scale division on the immersion refractometer has been worked out for several salts.

The effect of 1 per cent by volume of salt upon the density of an aqueous solution at 20° C. was determined for several salts.

Influence of Certain Organic Accelerators on Vulcanization of Rubber[1]

By George Stafford Whitby and Osman James Walker
McGill University, Montreal, Canada

The experiments recorded in this paper refer to the influence of 1 per cent of (*a*) piperidine piperidyl-dithiocarbamate,[2] (*b*) hexamethylenetetramine, and (*c*) thiocarbanilide on the rate of vulcanization of a 90:10 rubber-sulfur mix and on the tensile properties, vulcanization coefficients, and aging qualities of the vulcanizates produced.

The rubber employed was pale Hevea crêpe. The stocks were sheeted out to a thickness of about three-sixteenths of an inch.[3] Vulcanization was done in an oil bath provided with suitable stirring arrangements.[4] The rubber was enclosed in a mold consisting of two steel plates, the upper plate being 0.5 in., and the lower one, which contained a cavity for the reception of the rubber slab, being 0.8 in. thick. The upper and lower parts of the mold were fastened together by means of ten bolts and nuts, a thin gasket of lead foil and a small amount of a litharge-glycerol paste being used to secure oil-tightness. In order to allow for the heating up of the mold, the oil was raised, before the mold was introduced, to a temperature 20° above that at which it was desired to carry out the vulcanization.

After vulcanization, two dumb-bell test pieces were cut from each slab. One of these pieces was subjected to a tensile test after 3 days and the other 7 mo. later. For carrying out the tensile tests, sliding steel wedge-shaped grips, short enough to allow of the ends of the test piece projecting beyond the grips, were employed.[1] The dead weight method was used for applying the load. The loading was done in a uniform manner, measurements of elongation being made, on gage lines,[2] at definite intervals. Stress-strain curves were plotted.

The results obtained are shown in the accompanying tables and figures. The main series of vulcanizations on each mix was done at 141° (40 lb. steam). In the case of the control mix and of the mixes containing hexamethylenetetramine and thiocarbanilide, respectively, vulcanizations were also carried out at a higher temperature, *viz.*, 148° (50 lb. steam). In the case of the mix containing the piperidine salt, a second series of vulcanizations was carried out at a lower temperature, *viz.*, 130° (25 lb. steam), the rate of vulcanization being too high to allow of accurate experiments at 148°.

P_B represents the breaking stress in lb. per sq. in.; L^B the percentage length at break; $P_B \times L_B$ /100, the tensile product divided by 100, *i. e.*, the breaking stress referred to the cross section at failure, on the assumption that the volume remains unchanged; L_{750}, the percentage length at a load of 750 lb. per sq. in.; V. C., the vulcanization coefficient.

The stress-strain curves are shown only from a point corresponding to a length of about 400 per cent, as the later portion of the curve is the portion which can be determined most accurately and is all that is necessary in order to obtain the desired information as to relative rate of curve, breaking points, etc. The curves referring to tensile tests made 3 days after vulcanization are drawn with unbroken lines; those referring to tensile tests made after aging 7 mo. with broken lines. L_{750} forms a convenient reference point, the figures corresponding to which enable the relative positions of curves corresponding to different periods of vulcanization and the shifting of the curves on aging to be read easily.

TABLE I.—CONTROL (90 PARTS RUBBER : 10 PARTS SULFUR)

	Time, Min.	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V. C.		After Aging 7 mos. P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V. C.
				At 141°								
A	120	875	970	8487	951	2.27	A'	1040	930	9672	888	2.56
B	150	1160	930	10788	866	3.27	B'	1285	880	11335	813	3.59
C	180	1290	875	11288	800	4.31	C'	1280	827	10585	754	4.26
D	210	Brittle (broke at 150 lb. sq. in.)				4.97						
				At 148°								
E	75	930	950	8835	913	2.97	E'	1070	895	9576	836	3.23
F	90	1251	880	11008	802	4.41						

TABLE II.—CONTROL + 1 PER CENT PIPERIDINE PIPERIDYL-DITHIOCARBAMATE)

	Time, Min.	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V. C.		After Aging 7 mos. P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V. C.
				At 141°								
G	10	1125	913	10271	848	1.88	G'	1500	878	13170	779	2.03
H	15	1220	903	11017	827	2.09	H'	1457	853	12428	745	2.43
I	17.5	1315	870	11440	795	2.70	I'	1420	815	11570	730	2.91
J	22.5	1525	836	12760	714	3.65	J'	1803	805	14510	683	4.00
K	25	1870	845	15801	723	3.72	K'	1841	785	14452	661	4.15
L	30	1826	824	15047	702	4.40	L'	1738	751	13053	634	4.73
				At 130°								
M	45	1291	902	11644	830	2.60	M'	1302	872	11353	798	2.89
N	60	1657	874	14481	776	3.00	N'	1672	836	13978	740	3.55
O	75	1687	820	13834	723	3.73	O'	1769	804	14224	690	4.33
P	90	1654	800	13232	706	4.59	P'	2040	803	16381	636	5.10

TABLE III.—(CONTROL + 1 PER CENT HEXAMETHYLENETETRAMINE)

	Time, Min.	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V. C.		After Aging 7 mos. P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}
				At 141°							
Q	30	745	940	7000	940	3.64					
R	60	1148	959	11010	910	4.76					
S	75	1070	928	9929	884	5.28	S'	1292	880	11370	808
T	90	1312	935	12267	873	5.41	T'	1290	880	11352	808
U	105	1330	925	12302	862	5.69	U'	1362	865	11781	786
V	120	1336	910	12158	844	5.79	V'	1440	867	12485	778
				At 148°							
W	30	1087	970	10544	916	4.71					
X	45	1523	960	14621	880	5.32	X'	1500	880	13200	790
Y	60	1413	900	12717	823	6.07	Y'	1350	835	11272	749

---

[1] Presented before the Rubber Division at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] In the preparation of this compound the piperidine can conveniently be applied in the form of an aqueous solution.

[3] The authors are much indebted to Mr. W. B. Wiegand for making the mixings.

[4] The oil used was a light engine oil known in the Standard Oil system as Zone Oil.

[1] Cf. G. Stafford Whitby, "Plantation Rubber and the Testing of Rubber," 1920, 261, Longmans.

[2] In order to obtain these lines fine they were drawn while the rubber was stretched to twice its length. After his stretching the rubber was allowed to rest for some time before being tested.

TABLE IV. (CONTROL + 1 PER CENT. THIOCARBANILIDE.)

	Time, Min.	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V. C.	After Aging 7 mos.	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}
				At 141°							
I	120	680	920	6256	(930)	3.08	I'	686	800	5488	(813)
II	150	1050	937	9839	891	3.98	II'	1243	856	10640	780
III	180	1274	910	11593	819	4.87	III'	1390	847	11774	754
IV	195	1270	868	11024	791	5.21	IV'	1126	890	9098	737
V	210	Brittle (broke at 285 lb/sq.in.)				6.02	V'	Brittle broke at 228 lb/sq.in.)			
				At 148°							
VI	75	940	935	8780	901	3.41	VI'	1119	878	9824	821
VII	90	1118	890	9950	834	4.53	VII'	1485	860	12740	760
VIII	105	1270	850	10790	773	5.21	VIII'	1272	770	9563	700
IX	120					5.58	IX'	Brittle (broke at 240 lb/sq.in.)			

DISCUSSION OF RESULTS

CONTROL—The optimum cure at 141° is obtained at about 180 min. The maximal tensile strength shown by the rubber is lower than that usually shown in tests with first latex rubber, probably owing, in part at least, to the circumstance that the cross section of the test pieces used ($\frac{1}{2}$ × $\frac{3}{16}$ in.) was greater than usual. On aging the vulcanizates, the breaking points, the position of the stress-strain curves, and the magnitude of the vulcanization coefficients alter in a normal manner. The downward movement of the stress-strain curve on aging appears to be noticeably slower than that found by de Vries and Hellendoorn[1] in aging experiments at tropical temperatures with rubber samples cured, with 7.5 per cent of sulfur, at 148°.

Comparing vulcanization at 148° with vulcanization at 141°, it may be noticed that the curve for F (90 min. at 148°) is almost coincident with that for C (180 min. at 141°), showing that an increase in temperature of 7° roughly doubles the rate of vulcanization.

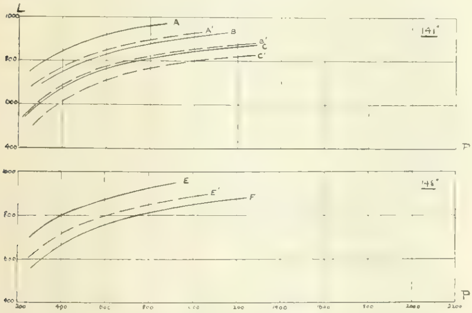


FIG. 1—VULCANIZATION OF CONTROL (90 RUBBER : 10 SULFUR) AT 141° AND AT 148°

PIPERIDINE PIPERIDYL-DITHIOCARBAMATE. *Rate of Cure*—The optimum period of cure at 141° may be considered as being 25 min. Hence the "acceleration factor"[1] of the piperidine salt may be considered as 180/25, *i. e.*, 7. Comparison of the vulcanization results at 130° with the results for the control at 148° shows that 1 per cent of the piperidine salt leads to vulcanization in a shorter period of time at 130° (25 lb. steam) than in its absence is required at 148° (50 lb. steam). (The optimum time at 130° may be taken as 75 min.)

Tensil Properties—The accelerator has an important effect in increasing the tenacity developed by the rubber on vulcanization, the maximal breaking stress developed (1870 lb. per sq. in.) being 45 per cent greater than that developed by the control (1270 lb. per sq. in.). The accelerator, however, reduces the extensibility. It has the further effect of bringing the optimum stress-strain curve into a lower position on the paper, L_B being 723 in the presence of the accelerator and 800 in its absence. These noteworthy effects of the accelerator, leading to a lower but longer stress-strain curve, may readily be seen by comparing Curve K, Fig. 2, with Curve C, Fig. 1.

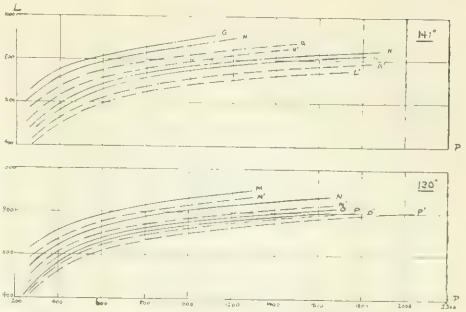


FIG. 2—VULCANIZATION WITH 1 PER CENT PIPERIDINE PIPERIDYL-DITHIOCARBAMATE AT 141° AND AT 130°

Coefficient of Vulcanization—The vulcanization coefficient at the optimum cure is somewhat reduced by the accelerator (3.72:4.31).

Aging—The aging qualities of vulcanizates prepared with the aid of the accelerator appear to be normal. They do not differ in any essential respect from those of the control or from those of rubber-sulfur vulcanizates in general as studied by deVries and Hellendoorn.[1] There is no evidence of the use of this vigorous accelerator leading to rapid deterioration. The curves move in a normal manner, and, if anything, at a slower rate than in the case of the control. In all cases L_B falls; P_B shows no serious falling off, and, in cures short of the optimum, it rises.

It is of interest to compare the effects of piperidine piperidyl-dithiocarbamate with those of other powerful accelerators for which data have been published. The dithiocarbamate prepared from piperidine, when tested in a mix containing rubber and sulfur only, is by no means as powerful as Cranor's results[2] show the corresponding compound prepared from dimethylamine to be when tested in a mix containing zinc oxide in addition to rubber and sulfur. Quite possibly, however, the piperidine compound would prove to be similar to the dimethylamine compound in its degree of activity if it were tested in the presence of zinc oxide. The results obtained with the piperidine compound in the absence of zinc oxide agree with the results obtained by Cranor with the dimethylamine compound in the presence of zinc oxide in the following respects: In both cases the accelerator raises the maximal breaking stress attainable, and this maximum corresponds to a lower stress-strain curve. They differ in the following respects: (1) According to Cranor's data, the dimethylamine compound does not reduce the ultimate elongation; (2) whereas the vulcanization coefficient at the optimum cure is very greatly reduced by the presence of the dimethylamine compound, it is reduced only to a comparatively small extent by the piperidine compound. This last difference is not unexpected, in view of the much greater degree of activity of the former compound when used in the presence of zinc oxide.

The piperidine salt has almost exactly the same degree

---

[1] *Arch. Rubbercultuur*, 4, 1920, 429.

[1] Compare Twiss and Brazier, *J. Soc. Chem. Ind.*, 39, 1920, 125.

[1] *Loc. cit.*

[2] *India Rubber World*, 1919, 137.

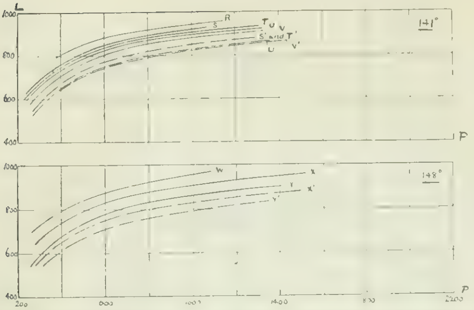


Fig. 3—Vulcanization with 1 per cent Hexamethylenetetramine at 141° and at 148°

of activity as aldehyde ammonia—an accelerator which has been extensively tested in a simple rubber-sulfur mix by Twiss and Brazier.[1] These authors give the "acceleration factor" of aldehyde ammonia as 7.5. A comparison of the effects of the piperidine salt and of aldehyde ammonia shows the following:

1—The effect on the vulcanization coefficient at the optimum cure is of the same order, a reduction, but not a very great one, being noticeable.

2—The effect on the position of the stress-strain curve and on the ultimate elongation at the optimum cure is similar, the curve lying lower and L_B being smaller than with the controls, although the effect of aldehyde ammonia in these respects is not quite so marked as that of the piperidine salt.

3—The piperidine salt appears to have a marked advantage over aldehyde ammonia in regard to the tensile strength of the vulcanizates; for, whereas the former greatly enhances the maximal tensile strength, the latter increases it only a little.

HEXAMETHYLENETETRAMINE. *Rate of Cure*—In these experiments hexamethylenetetramine appears as only a very mild accelerator; the rate of cure at 141° being only a little more than 1.5 times the rate shown by the control (say, 180: 105-120).

Tensile Properties—The ultimate elongation (L_B) shown by the rubber at the optimum cure is increased. The curve corresponding to the optimum cure is higher in the presence than in the absence of the accelerator by a length of about 50 per cent. The most striking effect of the accelerator on the tensile properties is to be seen in the slowness with which the tensile properties of the vulcanizates change over a rather wide range of curing intervals. The tensile strength, the ultimate elongation, and, as may be seen by a glance at Fig. 3, the position of the stress-strain curve, change only remarkably slowly. Whereas, in the case of the control, a reduction of one-third in the time of cure below the optimum (from 180 to 120 min.) shifts the curve (L_{750}) by 150 per cent, a similar reduction (from 120 to 90 min.) in the case of the mix containing hexamethylenetetramine shifts the curve only 29 per cent. Hence it would appear that the addition of hexamethylenetetramine to a pure gum stock has the effect of enabling the period of vulcanization to be varied over a comparatively wide range without much change occurring in the tensile properties of the resulting vulcanizates.

The maximal tensile strength developed is slightly, but not, as with piperidine piperidyl-dithiocarbamate, strikingly, greater than that developed by the control.

These conclusions as to the effect of hexamethylenetetramine on the tensile properties of rubber-sulfur vulcanizates are in general agreement with conclusions indicated by data published by Twiss and Howson[1] for the same accelerator. These authors, too, find the tensile strength maximum to be flat. They also find the position of the stress-strain curve (indicated by the length at 0.5 kg. per sq. mm.) to change more slowly in the presence than in the absence of the accelerator; although the difference is not so marked as in the present experiments. The results of Twiss and Howson show hexamethylenetetramine to be considerably more active in the presence of zinc oxide than in its absence, 1 per cent in the presence of zinc oxide having an acceleration factor of rather more than 2.[2] They also show that the flatness which is characteristic of the tensile strength maximum when the accelerator is used in the absence of zinc oxide is no longer to be seen when zinc oxide accompanies the accelerator.

Vulcanization Coefficient—Although hexamethylenetetramine accelerates the rate at which the optimum cure (as judged by tensile properties) is reached, it increases the amount of sulfur in combination at this cure. Whether this effect is due to the production of an acetone-insoluble material from the accelerator and sulfur cannot be said.

Aging—The vulcanizates prepared with hexamethylenetetramine behave normally during the aging period.

Comparison of the Effects of Piperidine Piperidyl-dithiocarbamate and Hexamethylenetetramine—The effects of these accelerators present a noteworthy contrast, which shows clearly how different properties may be conferred upon rubber by the use of different accelerators.

1—Whereas the piperidine salt diminishes the extensibility of the rubber, hexamethylenetetramine increases it. Further, the latter accelerator makes the rubber comparatively insensitive to changes in the time of vulcanization from the time giving the optimum cure, whereas the former accelerator has no such influence in altering the sensitiveness of the rubber to change in the vulcanization period.

2—Whereas the piperidine salt has a marked effect in increasing the tensile strength developed, hexamethylenetetramine has little or no such favorable effect.

3—Whereas use of the piperidine salt results in a reduction in the vulcanization coefficient at the optimum cure, hexamethylenetetramine results in an increase.

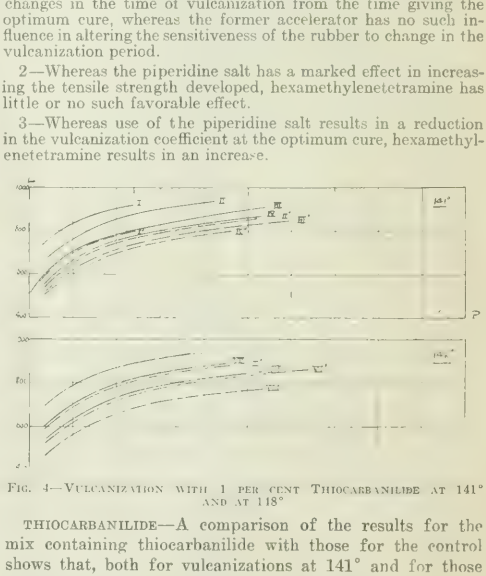


Fig. 4—Vulcanization with 1 per cent Thiocarbanilide at 141° and at 148°

THIOCARBANILIDE—A comparison of the results for the mix containing thiocarbanilide with those for the control shows that, both for vulcanizations at 141° and for those at 148°, the former results are substantially similar to the latter, as regards tensile properties. Hence, with respect to tensile properties, thiocarbanilide is without accelerating effect. The presence of thiocarbonilide in the pure gum stock in question leads, however, to some increase in the combined sulfur, the vulcanization coefficient at the 180-min. cure being raised from 4.31 to 4.87. This is in accord with results of Kratz, Flower and Shapiro.[1] It is possible that the apparent increase in the vulcanization coefficient is due to the formation of acetone-insoluble products as a result of interaction between sulfur, thiocarbanilide or its decomposition products, and, possibly, caoutchouc.

---

[1] Loc. cit.

[1] J. Soc. Chem. Ind., 30 (1920), 287t; Cf. also Twiss and Brazier, Ibid., 131t.

[2] Cf. also Cranor, *Loc. cit.* Cranor's results with hexamethylenetetramine also show the accelerator to be more active in the presence of zinc oxide than was found by Twiss and Howson or in the present experiments to be in the absence of the oxide. They also indicate that in the presence of zinc oxide the accelerator leads to ceratin irregularities in the manner in which the stress strain curve shifts on continued vulcanization. These irregularities have been examined more closely by Twiss and Howson (*Loc. cit.*)

The thiocarbanilide is without effect on aging.

SUMMARY

1—In a simple rubber-sulfur mix piperidine piperidyl-dithiocarbamate is a comparatively powerful, and hexamethylenetetramine a weak, accelerator, 1 per cent reducing the time of optimum cure to one-seventh and to two-thirds, respectively, of the time required in the absence of the accelerator.

2—These two accelerators present a notable contrast in their effects on the tensile properties of the rubber. The piperidine salt greatly enhances the tensile strength which can be developed; it leads to a smaller ultimate elongation and a lower position of the stress-strain curve (strains as ordinates) at the optimum cure. Hexamethylenetetramine enhances the tensile strength only a little; it leads to a greater ultimate elongation and a higher position of the stress-strain curve at the optimum cure; it also has the effect of causing the tensile properties to change with exceptional slowness with change in the length of the vulcanization period.

3—The piperidine salt reduces somewhat, whereas hexamethylenetetramine increases somewhat, the coefficient of vulcanization at the optimum cure.

4—In the absence of zinc oxide, thiocarbanilide is without accelerating effect on the vulcanization, considered with respect to tensile properties. It increases somewhat the vulcanization coefficient at the optimum cure.

5—In an aging test of 7 mo.' duration, pure gum vulcanizates prepared with the aid of the accelerators in question are found to age normally.

ADDENDUM. Vulcanization tests which Mr. Arnold H. Smith has kindly carried out with material supplied by the authors show that the presence of zinc oxide increases the accelerating activity of piperidine piperidyl-dithiocarbamate very greatly over that found, in the absence of zinc oxide, in the experiments recorded above. In a mixture similar to that used above, but containing in addition 10 per cent of zinc oxide, the acceleration factor for 1 per cent of the piperidine compound is in the neighborhood of 200; 1 mins. heating at 141° giving an over-cure, and a good cure being obtainable by 4 mins. heating at a temperature as low as 105° (3 lb. steam).[1]

[1] It is proposed to record more fully the data relative to these tests in the Correspondence column of a succeeding issue of THIS JOURNAL.

LABORATORY AND PLANT

A Combined Extractor, Reflux Condenser, Still and Autoclave[2]

By Alfred T. Shohl and Mathilde L. Koch

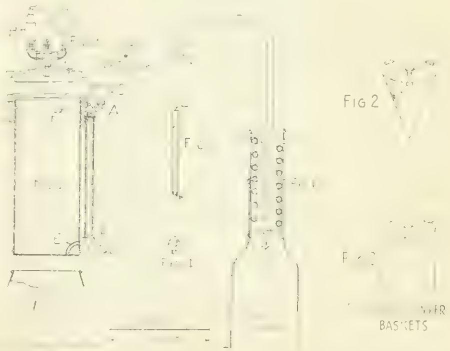
DEPARTMENT OF CHEMICAL HYGIENE, SCHOOL OF HYGIENE AND PUBLIC HEALTH, JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND

A good extraction apparatus to accommodate large amounts of material at a charge, an apparatus to make absolute alcohol, and an autoclave were needed in the laboratory. Because of limited funds available a single piece of apparatus was designed to meet these needs. In use it proved to be not only more economical, but also more efficient in several respects than any available apparatus.

It is a modification of an ordinary autoclave such as is used in sterilizing under pressure. A glass tube gage which is added shows the level of the contained fluid and has a charging funnel and a draw-off spigot. The autoclave is converted into a refluxing or extraction apparatus by unscrewing the blow-off valve and inserting the upright condenser. The condenser is of such a type that, by changing its position, it may be converted into a condenser for a still.

The apparatus consists of six parts: (1) The main body with lid, (2) extraction trays, (3) autoclave attachment, (4) a special fitting or stuffing box, (5) a connecting tube, and (6) a condenser with stand.

The main body (Fig. 1) of the apparatus consists of a riveted copper cylinder to which is soldered a seamless copper bottom. A glass tube gage connects to the body above and below through two 3-way stopcocks, A and B, and also above with a charging funnel, C, and below with a draw-off spigot, D. Thus fluid can be drawn off and fresh fluid added while the apparatus is in operation. The inner surface of the main body is heavily tinned. Connecting with the bottom entrance of the gage is a tinned tube, E, bent to reach nearly to the bottom so that the contained liquid may be syphoned off. Near the top are riveted three right-angled strips of metal, F, 0.5 in. wide and projecting 0.5 in. from the side. These are in the same horizontal plane and equidistant and are the supports for the extraction [illegible].



The extraction trays (Fig. 2) contain the ma[illegible] extracted. They may be either cylindrical or [illegible]

[1] THIS JOURNAL, 13 (1921), 130.

[2] Received April 29, 1921.

and are made of wire mesh or of tinned metal perforated with numerous small holes. The size of the holes depends on the nature of the material to be extracted. Three strips of metal converge from the upper edge to the center, and at the union there is a knob which serves both as a handle to pick up the tray and as a spreader to distribute the extracting fluid as it drops from the condenser.

The lid of the apparatus is of cast brass. This lid is seated on the cast brass ring which forms the top of the main body by means of a ground joint. It is held in place by six toggle bolts with wing nuts. There are two threaded holes through the lid. The central hole carries the autoclave attachment. The other is provided for a thermometer.

The autoclave attachment (Fig. 3) consists of a blow-off valve, G, which screws into hole O, and also, attached by right-angle side arms to the central tube carrying the blow-off valve, a safety valve, H, and a pressure gage, I. A special fitting or stuffing box (Fig. 4), with ground joint, of the same size and thread as the blow-off valve, can be screwed in place of the blow-off valve when the apparatus is used as an extractor, still, or reflux condenser. The ground joint, J, of Fig. 4 is tapered and is female. Into this nut fits a connecting tube. This connecting tube (Fig. 5) is of brass, lined with block tin. It has a ground male taper joint, K, at one end and a ground female taper joint, L, at the other, so that below it connects with the main body of the apparatus and above with the condenser.

The condenser (Fig. 6) is a block-tin, coiled pipe surrounded by a copper cylinder water jacket. One end of the pipe, M, extends a short distance below the condenser, while the other end, N, extends above the condenser in a rough semicircle. Both ends are tapered male ends. The water jacket fits into a stand made of two bands of strap iron held together by and resting on three legs. The heating is accomplished by gas or by an electric hot plate.

When the stand supporting the condenser is placed upon the lid of the main body, the legs of the stand interlock their feet with three of the wing nut clamps and thus hold the condenser in position. By inserting tube (Fig. 5), that is, fitting K into J and L into M, the apparatus is in position to be used as an extractor or as a reflux condenser.

When the condenser stand rests beside the apparatus with the upper end of the condensing tube N fitted into the tapering joint J, the apparatus is in position to be used as a still.

When the blow-off valve G is screwed into hole O, the apparatus is ready for use as an autoclave.

The apparatus is most satisfactory for the extraction of material either in the dry, powdered state or in the fresh, moist state, with the different fat solvents or with water. Without removing or disturbing the material, the solvent can be drawn off and fresh solvent added for reëxtraction. Then without cooling the extract can be concentrated and the solvent recovered by distillation. Absolute alcohol can be made from ordinary alcohol by refluxing the alcohol over lime, and the absolute alcohol can then be distilled without exposure to the air. Extraction or distillation can be conducted under either positive or negative pressure.

The advantages of this apparatus are that it is easily set up and readily transported; it is easy to clean, and, above all, simple to operate. Its greatest value is that it allows a combination of procedures such as refluxing and distilling, or extracting and distilling, in a single piece of apparatus.

Radiation Effects in Thermometry

By Clark S. Robinson[1]

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

A thermometer, pyrometer, or other temperature measuring device, when inserted in a gas for the purpose of measuring its temperature, does not, except under unusual conditions, record the true gas temperature, and the deviation may, in cases of high temperature, amount to several hundred degrees, and at ordinary temperatures it may be as much as ten or more degrees.

It has long been known that heat is transmitted by radiation in a similar manner to light, and that it can be reflected, refracted, and absorbed. That different substances have different radiating as well as different absorbing powers has also been known, and as early as 1814 Dr. William Charles Wells[2] performed many interesting experiments on these phenomena. However, while the effects of radiation on thermometer and pyrometer measurements of gas temperatures have been well known by physicists, it has not been common knowledge that thermometer or pyrometer measurements are subject to such deviations. Thousands of tests on furnaces, boilers, and the like have been made by engineers, in which gas temperature have been measured by the usual means, and furnace efficiencies calculated, when the temperatures thus measured may have been far from the fact. It is the purpose of this article to explain how true gas temperatures may be calculated, and to give the results of some experiments made by Mr. Goodman Mottelson in connection with his thesis on this subject at the Massachusetts Institute of Technology during the past year.

The Calculation of True Gas Temperatures

A thermometer or other temperature measuring instrument, when introduced into a gas, tends to approach the temperature of the gas. In order to do this it must receive heat, if the gas is at a higher temperature, or it must lose heat, if the gas is at a lower temperature. This flow of heat to or from the thermometer occurs in two ways, by conduction and convection between the gas and the thermometer, and by radiation between the thermometer and the surroundings, usually the walls of the chamber or flue. Imagine, for instance, a tube in a fire-tube boiler, through which hot furnace gases are passing, giving up part of their heat to the cooler walls of the tube. A pyrometer inserted in the tube, if at the gas temperature, would radiate heat to the cooler tube, which would lower the thermometer temperature. Heat would then flow into it from the gas, and when equilibrium was reached the pyrometer would be at a temperature sufficiently below gas temperature, yet sufficiently above tube temperature, so that its loss of heat by radiation to the tube would just compensate for the heat gained by conduction from the gas.

On the other hand, a thermometer inserted in the air between the tubes of a steam coil heater for air, where the heating tubes are hotter than the air, would indicate a temperature between that of the air and that of the hot surfaces, the thermometer reading too high where in the former case it would read too low.

The rate of flow of heat by conduction from the gas to the thermometer can be expressed by the equation

---

[1] Received June 24, 1921.

[2] An Essay on Dew, London, 1914.

$$\frac{Q}{\theta}=h_cA\,(T-t_t) \qquad (1)$$

where $\frac{Q}{\theta}$ = heat flow per unit time

h_c = coefficient of heat transfer by conduction, expressed in suitable units, such as B.t.u. per °F. temperature difference between gas and thermometer per hr.

T = air temperature, in °F. abs.

t_t = thermometer temperature, in °F. abs.

A = area of surface thermometer through which heat is flowing.

The rate of flow of heat by radiation from the thermometer to the surrounding walls can be expressed by the equation (in English units)

$$\frac{Q}{\theta}=R_t\times 0.162\times A\left[\left(\frac{t_t}{100}\right)^4-\left(\frac{t_w}{100}\right)^4\right] \qquad (2)$$

where R_t = black body coefficient of material from which thermometer is made.

t_w = temperature of surrounding walls, in F. abs.

At equilibrium Equations 1 and 2 are equal. Therefore,

$$h_c\,(T-t_t)=R_t\times 0.162\times\left[\left(\frac{t_t}{100}\right)^4-\left(\frac{t_w}{100}\right)^4\right] \qquad (3)$$

From this equation it is possible to calculate the true gas temperature, T, from the thermometer reading t_t, if the values of h_c, R_t, and t_w are known.

The heat transfer coefficient, h_c, can be calculated from the Beckett equation[1] when the gas is moving under forced draft:

$$h_c=\frac{0.44\,V^{0.8}T^{0.3}C_p\,(m-0.081)}{M^{0.1}(m-0.027)} \qquad (4)$$

where h_c = B.t.u./hr./sq. ft. of heating surface/°F. difference

V = lbs. of gas/sq. ft. of cross section of gas pass./sec.

T = temperature of gas in °F. abs.

Cp = specific heat of gas at constant pressure

m = mean hydraulic radius of the gas passage in ft.

M = molecular weight of the gas

When the gas is moving under convection currents only, Equation 6 is to be used.

The black body coefficient (R_t) for a number of substances are given approximately in the following table:

SUBSTANCE.	R.
Absolute black body	1.0
Highly oxidized iron	0.90
Polished copper	0.07 to 0.10
Oxidized copper	0.70
Monel metal	0.06
Gold, polished	0.05
Silver, polished	0.03
Nickel, polished	0.35
Platinum	0.24
Glass	0.90

For the wall temperature, t_w, when the walls are incandescent, the optical pyrometer may be used, or, for lower temperatures, thermocouples may be immersed in the wall surface. Where the wall temperature cannot be measured, another method, to be described below, may be used.

EXAMPLES

The following data were taken with a small electric furnace, 2-in. inside diameter, with the walls heated to approximately 725°C., as measured by an optical pyrometer. Thermometers were suspended just at the level of the open top of the furnace. Three thermometers were used, all of the usual mercury-in-glass laboratory type, and calibrated against each other. One of these was used as such, while the second had the bulb covered with a tightly fitting, polished silver shield, and the third was shielded with polished copper.

The following readings were made:

	UNSHIELDED ° C.	SILVER SHIELD ° C.	COPPER SHIELD ° C.
	255	158	179
	255	162	185
	261	162	185
	255	158	182
	263	160	181
	261	161	184
	265	162	178
	267	165	182
	265	163	177
	269	162	180
Aver.	261.6	161.3	181.3

Any motion of the air about the thermometers was due in this case to convection currents alone.

Calling t_t the temperature of the unshielded thermometer, and t_s that of the one with the silver shield, Equation 3 may be written for each as follows:

$$(T-t_t)\,h_c=R_t\times 0.162\left[\left(\frac{t_w}{100}\right)^4-\left(\frac{t_t}{100}\right)^4\right]$$

$$(T-t_s)\,h_c=R_s\times 0.162\left[\left(\frac{t_w}{100}\right)^4-\left(\frac{t_s}{100}\right)^4\right]$$

Eliminating t_w and solving for T

$$T=\frac{R_s\times 0.162\left[\left(\frac{t_t}{100}\right)^4-\left(\frac{t_s}{100}\right)^4\right]+\frac{R_s}{R_t}t_th_c-t_sh_c}{\frac{R_s}{R_t}h_c-h_c} \qquad (5)$$

The value for h_c may be calculated from the formula (English Units)

$$h_c=0.7+\frac{\Delta t}{375} \qquad (6)$$

which is for use when the flow of gas by a surface is due to convection currents only, Equation 4 being used for forced draft. In this case $\triangle t$ is the difference in temperature between the hot walls and the thermometers, and must be calculated for each one separately. Under the conditions, Equation 5 must be rewritten, using h_{ct} for the value of h_c for the unshielded thermometer and h_{cs} for the silver shielded one.

$$T=\frac{R_s\times 0.162\left[\left(\frac{t_t}{100}\right)^4-\left(\frac{t_s}{100}\right)^4\right]\times\frac{R_s}{R_t}t_th_{ct}-t_sh_{cs}}{\frac{R_s}{R_t}h_{ct}-h_{cs}}$$

$R_s=0.03$, $R_t=0.90$. $t_t=261.6°$ C. $=963°$ F. abs., $t_s=161.3°$ C. $=783°$ F. abs.

$$h_{ct}=0.7+\frac{(725-261.6)\times 1.8}{375}=2.9$$

$$h_{cs}=0.7+\frac{(725-161.3)\times 1.8}{375}=3.4$$

$$\therefore T=\frac{0.03\times 0.162\,[(9.63)^4-(7.83)^4]+\frac{0.03}{0.90}\times 963\times 2.9-783\times 3.4}{\frac{0.03}{0.90}\times 2.9-3.4}$$

$T=772°$ F. abs. $=155°$ C.

It will be noted that the silver thermometer under these conditions read 6° C. too high, while the plain glass one read 107° C. too high. The copper covered thermometer gave an intermediate reading, since its value of R_t is between that of silver and glass, that is, 0.07 to 0.10.

Another experiment was made with the same electric furnace to show the effect of various shields for thermometers.

	Unshielded Thermometer °C.	Silver Shield °C.	Black Iron Shield °C.	Glass Shield °C.
	272	169	313	292
	281	174	316	297
	275	171	316	299
	279	164	312	299
	284	166	316	297
Aver.	278	169	315	296

---

[1] M. I. T. Thesis 1920.

The shields were then removed, giving the following readings, the thermometers remaining in practically the same positions as before.

	287	290	282	272
	277	291	280	260
	281	290	293	266
	281	293	284	263
	281	**292**	**293**	**263**
Aver.	281	291	286	265

The following data were obtained in a heated galvanized pipe 12 in. in diameter, through which a warm mixture of air and burner gases was passing at the rate of 2.3 lbs. per sq. ft. of cross-section of the pipe per second.

Silver thermometer = 123°, 126°, 124° C. Aver. = 124° C.
Plain thermometer = 152°, 150°, 149° C. Aver. = 150° C.

Using Equation 4, h_c was found to be 3.0 in English units.

$$h_c = \frac{0.44\times(2.3)^{0.8}\times(715)^{[illegible]}\times0.24\times(0.25-0.081)}{(30)^{[illegible]}\times(0.25-0.027)} = 3.0$$

using for T the value 715 obtained from the reading of the silver thermometer as being near the true temperature, a small error in this temperature being negligible. Using Equation 5,

$$T = \frac{0.03\times0.162\left[\left(\frac{150\times1.8+492}{100}\right)^4-\left(\frac{125\times1.8+492}{100}\right)^4\right]+\frac{0.03}{0.90}\times(762-715)\times3.0}{\frac{0.03}{0.90}\times3.0-3.0}$$

T = 712° F. abs. = 122° C.

In this case, the silver thermometer read 2° C. too high, and the glass one 28° too high.

Two thermometers, one silver and the other plain, were inserted in the intake manifold of a gasoline engine whose intake gases had been previously heated, and which were moving at a high velocity, 7.5 lbs. per sq. ft. per sec. Under these conditions, the value of h_c was great enough nearly to overcome the effect of radiation, and the two thermometers read the same at 60° C.

Tests were made in a galvanized iron pipe 7 in. in diameter, in which burner gases containing some sulfur dioxide were flowing at the rate of 0.125 lbs. per sq. ft. per sec. The silver became tarnished during the test, and its reading fell off somewhat, as is shown in the following table:

Silver	292	292	290	292	293	256	253	251	248° C.
Plain	276	277	278	278	278	247	245	243	241 C.
Difference	16	15	12	14	15	9	8	8	7° C.

The tarnished silver was then compared in a heated pipe with a thermometer shielded with polished monel metal.

Tarnished silver	188	188	183	185	187	189	189	192
Average = 188° C.								
Monel metal	186	185	180	170	179	182	185	189
Average = 183° C.								
Plain glass	276	274	280	278	278	286	287	288
Average = 281° C.								

The silver shield was then polished and compared again with monel metal, the gas velocity having changed.

Polished silver	174	175	177	178	177	178	170	169
Average = 173° C.								
Monel metal	195	199	204	204	204	205	201	204
Average = 202° C.								
Plain glass	283	285	283	277	290	282	287	287
Average = 284° C.								

CONCLUSIONS

1—Thermometers for measuring gas temperatures must have their readings corrected for the effect of radiation to the surroundings.

2—For measurements permitting small errors, a silver shield will give fairly close approximations if uncorrected. It is necessary, however, to correct the silver thermometer reading in order to get accurate temperatures.

3—For corrosive gases monel metal can be used in place of silver, but the reading should be corrected except for very approximate work.

4—Where gas is moving at very high velocity, any thermometer will read practically the true temperature, the large deviations occurring where the gas velocities are very low.

5—Thermometers will read true gas temperature exactly only when the surrounding walls are at the same temperature as the gas.

BIBLIOGRAPHY

Henry A. Hazen, "Thermometer Exposure," U. S. Army, Signal Corps.
Le Chatelier, "High Temperature Measurements."
Steinmetz, "Radiation, Light, and Illumination."
Tyndall, "Heat a Mode of Motion."
W. C. Wells, "An Essay on Dew."
W. K. Lewis, "Chemical Engineering Notes."

ADDRESSES AND CONTRIBUTED ARTICLES

The Chemistry of Acenaphthene and Its Derivatives[1, 2]

By Dorothy A. Hahn and Harriet E. Holmes
Mt. Holyoke College, South Hadley, Massachusetts

The purpose of this paper is to present an outline of the chemistry of acenaphthene, accompanied by a fairly complete bibliography of the substance. Such an outline has not as yet been attempted, and it seems desirable because of the fact that it may serve to call attention to the many gaps which exist in the chemistry of this very interesting substance and thus may lead to a thorough and systematic investigation of its derivatives. In this connection it may be pointed out that within recent years methods for separating acenaphthene from coal tar have been perfected so that it is no longer the rare and expensive preparation which it was when the first systematic investigation of its derivatives was undertaken by C. Graebe[3] and his co-workers in Germany and by T. Ewan and J. B. Cohen[1] at about the same time in England. The research initiated by these men was neglected for a period of seven years, when F. Sachs and G. Mosebach[2] entered the field with the avowed purpose of systematically filling in the gaps in the chemistry of acenaphthene. These investigators point out in the introduction to their second paper that the extreme meagerness of the information which exists in regard to the chemistry of acenaphthene is very surprising in view of the fact that the chemistry of napthalene, to which it is so closely related, has been brought to a state of dazzling completeness. The very fact that so many derivatives of naphthalene have been prepared and their constitution exactly determined is, however, of the greatest importance for the future development of acenaphthene chemistry. This fact will be referred to again later in this paper, but at the present time it need only be pointed out that by the appli-

---

[1] Received June 20, 1921.

[2] The work represented in the compilation of this material was done in partial fulfilment of the requirements for the degree of M.A. at Mt. Holyoke College. Acknowledgment must be made to Dr. G. C. Bailey, Director of Organic Research [illegible] of The Barrett Company, for the suggestion [illegible] this time.

[3] C. Graebe, *Ber.*, 20 (1887), 657; C. Graebe and E. Gfeller, *Ber.*, 25 (1892), 652; *Ann.*, 276 [illegible] and J. Jequier, *Ann.*, 290 (1896), 195; C. Graebe, *Ann.*, 327 (1903), 77.

[1] *J. Chem. Soc.*, 55 [illegible]

[2] *Ber.*, 43 (1910), 2473; 44 [illegible]

cation of a method developed by Graebe[1] in 1903, derivatives of acenaphthene may be readily transformed into the corresponding derivatives of naphthalene, thus affording a direct and easy method for the definite identification of new compounds.

The practical aspects of the chemistry of acenaphthene have also been emphasized by Sachs and Mosebach, who call attention to the fact that the recent discovery of such valuable dyes as Ciba Scarlet G, Thioindigo Scarlet 2G, and Ciba Red R[4] make a thorough investigation of the substitution products of acenaphthene increasingly desirable. Unfortunately the task which Sachs and Mosebach set for themselves has only been begun, and the investigation even of those substances which have been described has not been completed.

In summary it may be said that this field offers considerable attraction for research since the orientation of new derivatives may be readily elucidated and since acenaphthene itself is now available in the United States.[5] The present article aims to present the chemistry of the hydrocarbon in such a way as to emphasize the many gaps which exist in the literature relating to acenaphthene and its derivatives in the hope that a realization of the vast amount of work still to be done may stimulate American chemists to further research in this field.

OUTLINE OF TREATMENT OF SUBJECT

The various topics to be considered will be arranged in the following order: The discovery of acenaphthene and its relation to acenaphthylene will first be described. The hydrogenation, pyrogenic syntheses, the thermo- and photochemical transformations of the substance, and its various addition products will then be reviewed briefly. This will be followed by a few general remarks in regard to the constitution of acenaphthene, acenaphthylene, and some of the more important oxidation products which have been obtained from these substances. The possibilities of isomerism among the substitution products of acenaphthene will be considered, together with methods for identifying the different compounds according to the general method developed by Graebe. A systematic study of the halogen, nitro, amino, hydroxy, and sulfonic acid derivatives of acenaphthene will follow. Finally a careful analysis of methods of oxidation and a systematic review of the various products of oxidation will be attempted. The chemical properties and commercial applications of these substances will be considered in some detail, and in all cases where patents have been issued the fact will be noted. In this connection acknowledgment must be made to The Barrett Company for their courtesy in allowing the use of abstracts covering all patents mentioned in this paper.

Methods have been developed for the synthesis of substituted acenaphthenes,[6] but the products which have been obtained in this way will not be considered in the present survey of the chemistry of acenaphthene.

DISCOVERY OF ACENAPHTHENE AND ITS RELATION TO ACENAPHTHYLENE

Acenaphthene, $C_{12}H_{10}$, was discovered by Berthelot, who succeeded in isolating it from coal tar,[1] and who also prepared it by the action of acetylene upon naphthalene at the red heat.[2] The formula determined by Berthelot was later verified by C. Graebe[3] as a result of vapor density determinations. Further investigation of the chemistry of the substance by Berthelot and Bardy led to its synthesis by heating ethylnaphthalene at red heat.[4] The pioneer work of these earlier investigators was confirmed by that of A. Behr and W. A. van Dorp,[5] who also succeeded in establishing a definite relationship between this hydrocarbon and a very closely related, but less saturated compound, $C_{12}H_8$, which they called acenaphthylene. The discovery of the latter substance led to a number of experiments which involved the hydrogenation and halogenation of both hydrocarbons, and which were made the subject of investigation by M. Blumenthal,[7] by E. Bamberger and W. Lodter, and by C. Liebermann and L. Spiegel.[8] This work was, however, of very little importance, except in so far as it tended to establish somewhat more definitely the relationship between acenaphthene and acenaphthylene, since the compounds which were prepared in this way were not always pure chemical individuals and, even in cases where they were, their exact constitution was not established.

The first really systematic and exact work on acenaphthene was that of Graebe and his co-workers. These investigations will be reviewed in some detail, but before proceeding to their consideration the fact should be noted that interest in the hydrogenation[9] and in the pyrogenic syntheses[10] of acenaphthene have continued up to the present time. Indeed photo- and thermochemical changes have come definitely to be recognized as playing an extremely important role in the chemistry of acenaphthene. The extended investigations of Dziewonski and his co-workers can only be mentioned in this connection.[11]

The separation of chemically pure acenaphthene from coal tar presented many experimental difficulties, in view of the fact that the hydrocarbon possesses the power of forming addition products with an unusually large number of other compounds. This property seems to extend to at least some of its derivatives, with the result that unstable compounds or eutectic mixtures arise. Since these substances frequently possess more or less constant melting points and boiling points their formation is often confusing and harassing to the investigator. In certain instances, however, as in the case of the picrates, such addition products may be utilized for the separation or identification of the hydrocarbon in question. The extent to which investigations along these lines have been carried can only be indicated.[12]

---

[1] *Ann.*, **327** (1903), 77.

[2] Ciba Scarlet G, Basler chemischen Fabrik, D R P, 20[illegible],377

[3] Thioindigo scarlet 2G, Kalle and Co.

[4] Ciba Red R, M.L.B.

[5] Acenaphthene may be obtained in small lots for research purposes by application to the Research Department of The Barrett Company.

[6] [illegible] C. Graebe, "The Synthesis of Substituted Acenaphthylenes," *Ann.*, **327** (1903), 77; L. Beschke, *Ann.*, **369** (1909), 157, 184; M. Freund and K. Fleischer, "Synthesis of the Higher Indandiones," *Ann.*, **373** (1910), 291; **399** (1913), 182; **402** (1913), 51; C. Graebe, *Ann.*, **327** (1913), 77.

---

[1] *Jahresber*, **1867**, 594.

[2] *Bull. soc. chim.*, **9** (1868), 265.

[3] *Ber.*, **5** (1872), 15.

[4] *Bull. soc. chim.* [2] **18** (1872), 231.

[5] *Ber.*, **6** (1873), 753.

[6] *Ber.*, **7** (1874), 1092.

[7] *Ber.*, **20** (1887), 3073; 21 (1888), 836.

[8] *Ber*, **22** (1889), 779.

[9] P. Sabatier, *Bull. soc. chim*, [3] **25** (1901), 610, 671, 678; *Compt. rend.* **132** (1901), 1254; M. Padoa and W. Fabris, *Atti. accad. Lincei*, [5] **17** (1908), I, 111; W. N. Ipatiff, *Ber.*, **42** (1909), 2092.

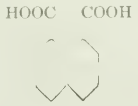
[10] R. Meyer and A. Tazen, *Ber.*, **46** (1913), 3183; J. E. Zanetti and G. Egloff, THIS JOURNAL, **9** (1917), 474; R. Meyer and W. Meyer, *Ber.*, **51** (1918), 1571.

[11] Dziewonski, *Ber.*, **36** (1903), 962; P. Rehlander, *Ber.*, **36** (1903), 1583; Dziewonski, *Ber.*, **45** (1912), 2491; **46** (1913), 1986; **47** (1914), 1679, 2680; **48**, 1915), 1917; **51** (1918), 457.

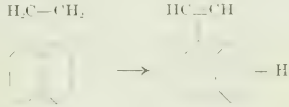
[12] Berthelot, *Compt. rend.*, **102** (1886), 1211; W. R. Hodgekinson, *Proc. Chem. Soc.*, **12** (1896), 110; C. L. Speyers, *J. Am. Chem. Soc.*, **18** (1896), 146; W. H. Perkins *J. Chem. Soc.*, **69** (1896), 1025; G. Pellini, *Gazz. chim. ital.*, **31** (1901), I, 1; E. Billows, *Z. Kryst Mineralog.*, **37** (1903), 396; **38** (1904), 505; G. Schultz,

THE CONSTITUTION OF ACENAPHTHENE AND CERTAIN OF ITS DERIVATIVES

Fairly large quantities of acenaphthene became available in 1873, when it was observed to separate in the form of flat prisms from tar distillates collected between the temperatures of 250° and 300°. The substance obtained in this way on recrystallization from alcohol gave a relatively pure product which melted between 94° and 96° and which boiled between 277° and 279° (uncorr.).[1] This discovery marks the beginning of a more exact investigation of the chemical properties of the substance. Acenapthene readily loses two atoms of hydrogen to form acenaphthylene and on further oxidation gives naphthalic acid. The latter fact was used to establish the exact constitution of acenaphthene. It was found, for example, that the crystalline product melting at 266° which is formed by the action of potassium bichromate and sulfuric acid upon acenaphthene was identical with an acid having the same formula, $C_{12}H_8O_4$, and the same properties, which had been synthesized by E. Bamberger and M. Philipp[2] from Estrand's nitronaphthalic acid. Since the latter had been identified as an *α-δ* or peri-derivative of naphthalene, the corresponding dicarboxylic acid was assumed to have the configuration

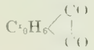


and from this it followed that the relationship between acenaphthene and acenaphthylene must be expressed in the following manner:

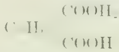


This conclusion was confirmed many years later by Baly and Tuck[3] as a result of their investigations upon the absorption spectra of naphthalene and acenaphthene.

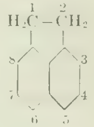
The solution of the problem as to the constitution of acenaphthene served at once to elucidate the relationship of acenaphthene to other of its oxidation products which were formed simultaneously with naphthalic acid. When oxidation was carried out, for example, in acetic acid by means of chromic oxide a crystalline compound melting at 232° was obtained. On analysis this was found to correspond to the formula, $C_{12}H_6O_2$. Its constitution was assumed to be


$$C_{10}H_6\left\langle\begin{matrix}CO\\ |\\ CO\end{matrix}\right.$$

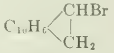
since on oxidation with potassium permanganate it was readily converted into naphthalic acid,[4]


$$C_{10}H_6\left\langle\begin{matrix}COOH\\ COOH\end{matrix}\right.$$

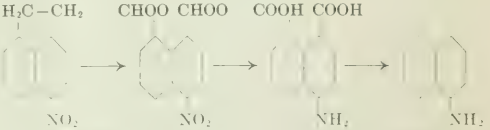
The discovery of these relationships paved the way, moreover, for the development of a general method by means of which it is now possible to determine the position taken by different substituents in the various derivatives of acenaphthene. According to the nomenclature adopted by F. Sachs and G. Mosebach,[1] all derivatives of acenaphthene may be regarded as representing substitutions in the following formula:



From this it is apparent that four different monosubstitution products of acenaphthene are possible, of which three represent substitution in the naphthalene ring. On the basis of theory, seventeen disubstitution products are possible if the entering groups are alike, and of these nine represent compounds in which both substituents are present in the aromatic part of the molecule. It will be shown later in this paper that these theoretical possibilities have not as yet been realized in the case of any single type of acenaphthene derivative. As early as 1874, however, Blumenthal[2] found it convenient to employ oxidation reactions in order to distinguish between compounds in which the hydrogen of the methylene groups had been replaced and those in which the substituent occupied a position in the naphthalene ring. If, for example, a substance having the formula $C_{12}H_9Br$ gave naphthalic acid upon oxidation it was assumed to possess the formula


$$C_{10}H_6\left\langle\begin{matrix}CHBr\\ |\\ CH_2\end{matrix}\right.$$

This very crude method was later perfected by C. Graebe[3] who, as the result of some very brilliant work, was able to assign exact formulas to monosubstituted nitro, bromo, acetyl, and benzoyl derivatives of acenaphthene. All of the substances under investigation by Graebe at this time were found to give *α*-substitution products of naphthalene, and from this it followed that these respective groups occupied the 5-position in acenapthene. For example, Graebe was able to establish the constitution of Quincke's nitroacenaphthene by converting it into *α*-naphthylamine as a result of the following transformations:



The constitutions of only a very few monosubstitution products of acenaphthene have been established with certainty. They include those which have just been mentioned, *viz.*, 5-nitro-, 5-bromo-, 5-acetyl-, and 5-benzoylacenaphthene, and one or two others which can be dismissed almost as briefly. For example, 5-nitroacenaphthene gives the corresponding amino compound upon reduction, and this in turn yields halogen derivatives when treated according to the Sandmeyer reaction. A 5-carboxyl derivative has also been obtained and identified. All

---

and K. Wurth, *J. Gasbel.* **48** (1905), 125, 152, 177, 200; H. Haakh, *Ber.*, **42** (1909), 4594; G. S. [illegible], *J. Chem. Soc.*, **93** (1908), 2098; A. Buguet, *Compt. rend.*, **149** (1909), 857; D. Tyler, *J. Chem. Soc.*, **97** (1910), 2620; O. Morgenstern, *Monatsh*, **31** (1910) 285; I. Cstromisslensky, *J. prakt. Chem.* [2] **84** (1911), 495; J. J. Sudborough, *J. Chem. Soc.*, **109** (1916), 1339; M. Cina, *Gazz. chim. ital.*, **45** (1915), II, 348; A. Kauffmann, *Ber.*, **50** (1917), 336; M. Cina, *Gazz. chim. ital*, **46** (1916), I, 289; P. Kremann, *Monatsh.* **40** (1919), 189.

[1] A. Behr and W. A. van Dorp, *Ber.*, **6** (1873), 60.

[2] E. Bamberger and M. Philipp, *Ber.*, **20** (1887), 237.

[3] *Proc. Roy. Soc.*, **24** (1908), 223; *J. Chem. Soc.*, **93** (1908), 102.

[4] C. Graebe, *Ber.*, **20** (1887), 657.

[1] *Ber.*, **44** (1911), 2852.

[2] *Ber.*, **7** (1874), 1092.

[3] *Ann.*, **327** (1903), 77.

[4] Compare N. Brione's Dissertation, Genf. 1893; also M. Guinsbourgs Dissertation Genf. 1894, and P. Haas's Dissertation, Freiburg, 1901.

other monosubstitution products, as well as a large number of the higher substitution products, of acenaphthene which have been described in the literature possess structures which are more or less uncertain, since their exact constitutions have not as yet been accurately determined according to the method developed by Graebe.

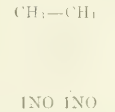
Halogen Derivatives

Halogen derivatives of acenaphthene were first investigated by Blumenthal,[1] who studied the action of halogen upon acenaphthene and acenaphthylene under a variety of different conditions. Several different compounds containing a halogen are mentioned, but most of these are of such doubtful purity as to leave their chemical constitution very much in question. Among them, however, is to be found a white crystalline compound which is described as melting at 52° to 53° and to which the probable formula

is given. These investigations were followed by others equally indefinite by J. T. Kebler,[2] E. Bamberger,[3] and T. Ewan.[4]. In all of these cases it seems probable that the separation of pure products was handicapped by the presence of eutectic mixtures, so that it was not until 1903 that perfectly pure 5-bromo-acenaphthene was isolated.[5] This substance corresponds to the compound described by Blumenthal and was obtained in excellent yields by a modification of his method. The corresponding chlorine derivative was prepared by H. Crompton[6] by an application of the same method. Crompton's later investigations were directed toward the study of other halogen derivatives of acenaphthene and of their oxidation products,[7] and included important data in regard to the freezing points of eutectic mixtures. In this connection it should be noted that the spectrochemical behavior of the halogen derivatives of acenaphthene has been studied by J. E. Purvis[8] and by K. von Auwers.[9] In 1910 the constitutions of 5-chloro-, 5-bromo-, and 5-iodo-acenaphthene were confirmed by F. Sachs and G. Mosebach, who succeeded in preparing these substances from 5-amino-acenaphthene.[10]

Nitro Derivatives

The nitration of acenaphthene was first investigated by F. Quincke,[11] when a mixture, consisting of two substances which were later identified as 5-nitro-acenaphthene and 5,6-dinitro-acenaphthene, was obtained. It is to be noted that under what seem to be very much the same conditions, E. Jandrier[12] obtained a mono-nitro derivative melting at 155°. The results described by Quincke have been confirmed by N. Briones[13] and by C. Graebe.[14] The latter succeeded in so modifying the procedure as greatly to improve the yield and was the first investigator to prepare a perfectly pure product, melting at 106° (Compare Quincke, 101° to 102°). The method of Graebe was later slightly modified by F. Sachs and G. Mosebach, who detail experiments by means of which yields averaging 84 per cent of theory were obtained. These investigators[1] also succeeded in improving the yield of 5,6-dinitro-acenaphthene (40 per cent) and in definitely establishing its constitution:



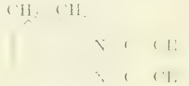
They have also prepared 4-nitro-5-amino- and 4-nitro-5-oxy-acenaphthene as a result of nitrating the acetyl derivatives of 5-amino-acenaphthene.

Amino Derivatives

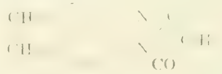
The reduction of nitro derivatives of acenaphthene has been effected by the application of a variety of different methods.[2] The best yields have been obtained by Sachs and Mosebach, who claim 77 per cent of theory in the case of 5-amino-acenaphthene against 50 per cent yields by Graebe and still smaller yields by all earlier methods. According to Sachs and Mosebach the acetyl derivative of 5-amino-acenaphthene shows a melting point of 192°, as against 185° (Graebe) and 174° (Quincke). 5-Amino-acenaphthene has been made the starting point in the preparation of a number of interesting derivatives, among which are 4-nitro-5-amino-acenaphthene, 4-nitro-5-oxy-acenaphthene, and 4,5-diaminoacenaphthene. 5,6-Diamino-acenaphthene has been obtained by reducing the corresponding dinitro derivative.

In conclusion it may be noted that the chemistry of the amino derivatives of acenaphthene is at the present time very incompletely developed. This is the more striking because of the number of possibilities for research which these compounds afford. For example, mono-amino derivatives may be diazotized and the resulting diazo compounds may then be coupled in a great variety of ways. Acenaphthene-azo-β-naphthol

has, for example, actually been obtained from 5-amino-acenaphthene in this manner.[3] The diamino derivatives, of which seventeen are theoretically possible while only two have actually been prepared, afford an opportunity for still other lines of work. For example, 4,5-diamino-acenaphthene has been observed to condense with diacetyl in alcohol solution to give



while 5,6-diamino-acenaphthene has been found to yield a number of different products under the action of carbonyl oxygen. The same substance reacts readily with phthalic anhydride to give



and with formic acid to give a somewhat similar compound, *viz.*,

---

[1] *Ber.*, **7** (1874), 1092.

[2] *Am. Chem. J.*, **10** (1888), 217.

[3] *Ber.*, **21** (1888), 836.

[4] *J. Chem. Soc.*, **55** (1889), 591.

[5] *Ann.*, **327** (1903), 85.

[6] *Proc. Chem. Soc.*, **24** (1908), 241.

[7] *Proc. Chem. Soc.*, **26** (1910), 226; **28** (1912), [illegible]; *J. Chem. Soc.*, **101** (1912), 1315; **103** (1913), 1302.

[8] *J. Chem. Soc.*, **11** (1912), 1315.

[9] *Ber.*, **46** (1913, 2988.

[10] *Ber.*, **43** (1910, 2473.

[11] *Ber.*, **20** (1887), 609; **21** (1888), 1454.

[12] *Compt. rend.*, **104** (1887), 1858.

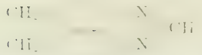
[13] *Bull. soc. chim.*, (3) **14** (1895), 116.

[14] *Ann.*, **327** (1903), 80.

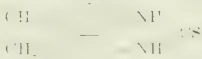
[1] *Ber.*, **44** (1911), 2860.

[2] Compare Quicke, *Ber.*, **21** (1888), 1456; Grabe, *Ann.*, **327** (1903), 81; H. Crompton, *J. Chem. Soc.*, **27** (1911), [illegible]; F. Sachs and G. Mosebach, *Ber.*, **43** (1910), 2473; **44** (9111), 2852.

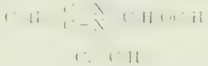
[3] Sachs and Mosebach, *Lo* [illegible]



Moreover, when 5,6-diaminoacenaphthene[1] is gently warmed with carbon bisulfide it reacts to give



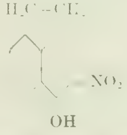
A number of observations in regard to the products which are formed by the condensation of acenaphthenequinone with aromatic diamines suggests the possibility that this type of reaction might yield interesting results if applied to the diamino derivatives of acenaphthene itself. For example, Liebermann and Zsuffa have observed that acenaphthenequinone combines readily with 5-ethoxy-2-amino-diphenylamine to form a product



which reacts with woolen fabrics to produce a yellow dye. The possibilities represented by this type of reaction become apparent from a consideration of the fact that acenaphthenequinone has been found to react readily with amino hydrogen in a number of other different compounds. For example, its action when condensed with amines, with hydrazines, and with hydroxylamines has been made the subject of investigation by G. Ampola and V. Recchi,[3] L. Behrend,[4] J. Hermes,[5] K. Auwers,[6] F. Ullmann and E. Cassirer,[7] A. Cruto,[8] G. Charrier,[9] L. Fransconi and F. Pirazzoli,[10] and certain of the observations along these lines have been deemed of sufficient commercial importance to cover by patents.[11] Ortho-oxy-aryl hydrazines, for example, condense with ortho-diketones, acenaphthenequinone, etc., to give products which dye wool different colors varying from orange to red to green. It should be borne in mind, moreover, in this connection that the original methylene groups present in acenaphthene remain unchanged in all compounds which result from reactions which involve the amino hydrogen of mono- and diamino derivatives of acenaphthene, and that the existence of methylene groups in condensation products of this type suggests the possibility of a variety of further reactions.

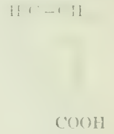
HYDROXY DERIVATIVES

Very little work has as yet been done upon these hydroxy derivatives of acenaphthene which represent substitution of ring hydrogen, and at present only three have been mentioned in the literature. 5-Oxy-4-nitroacenaphthene,



and the corresponding 5-oxy-4-amino derivative have been described by Sachs and Mosebach,[1] while the preparation of 5-acenaphthol is covered by patent.[2] Patents also exist[3] which describe the preparation of indigoid dyes by condensing 5-oxyacenaphthene or its derivatives with the usual reagents. The chemistry of those hydroxy derivatives of acenaphthene which result from the substitution of methylene hydrogen will be discussed fully in connection with the oxidation products of acenaphthene.

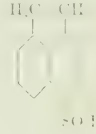
A number of investigations have been undertaken with the aim of substituing a carboxyl group for a ring hydrogen atom in acenaphthene. Berthelot[4] tried treating acenaphthene with phosgene and was unsuccessful. E. P. Harris[5] used chlorocarbamic acid and obtained an acid amide as the immediate product of the reaction. This when hydrolyzed gave acenaphthoic acid, m. p. 217°.



The same substance was prepared by C. Liebermann[6] by the direct action of oxalyl chloride upon acenaphthene (yield 30 per cent) and by Grignard,[7] both by the action (*a*) of CO_2 upon the magnesium derivative of acenaphthene and (*b*) by the hydrolysis of the nitrile. The latter was obtained by treating 5-bromo-acenaphthene with magnesium and cyanogen chloride. The acid which is prepared in these different ways is the only compound of its class which has been investigated up to the present time.

SULFONIC ACID DERIVATIVES

Very little is known in regard to the action of sulfuric acid upon acenaphthene and only two sulfonic acid derivatives are described in the literature. One of these substances was obtained by E. Oliveri-Mandala[8] as a result of heating acenaphthene with an equal weight of concentrated sulfuric acid on the water bath for 2 hrs. and then at 115° to 120° for half an hour. The following formula was assigned to the product:



The preparation of the other acid is covered by a German patent[9] and involves the formation of a monosulfonic acid derivative of acenaphthene in which a hydrogen atom of the methylene group has been substituted. This acid was obtained by the action of chlorosulfuric acid at a temperature ranging between 15° and 20° and is described as being very reactive in the presence of halogen and of oxidizing agents.

---

[1] Compare Sachs and Mosebach, *Ber.* 44 (1911), 2852.

[2] *Ber.*, 44 (1911), 852.

[3] *Atti accad. Lincei*, 8 (1899), 209.

[4] *J. prakt. Chem.* [2] 60 (1899), 1.

[5] Dissertation, Kiel, 1898.

[6] *Ann.*, 378 (1910), 210; also compare A. Cruto, *C. A.*, 10 (1916), 1857, and G. Charrier, *C. A.*, 10 (1916), 1172.

[7] *Ber.*, 43 (1910), 439.

[8] *Gazz. chim. ital.*, 45 (1915), II, 324.

[9] *Ibid.*, 45 (1915), I, 516.

[10] *Gazz. chim. ital.*, 33 (1903), I. 36.

[11] Compare Holiday and Hodgekinson Brit. Patent 3730 (1883); M.L.B., D.R.P. 258,099; Leonhardt and Co., D.R.P. 258,017; Basler chemischen Fabrik, D.R.P. 218,992 (1910).

[1] *Loc. cit.*

[2] Elberfelder Farbenfabriken, See *Ber.*, 44 (1911), 2860.

[3] F. Bayer and Co., D.R.P. 237,199, 237,266, 241,825, 241,826 and 241,827. Also compare Brit. Patent 3730 (1818), which corresponds to D.R.P. 237,266.

[4] *Bull. soc. chim.* [2], 13 (1870), 391.

[5] Gattermann, *Ann.*, 244 (1888), 29; E. P. Harris, Dissertation Gottingen, 1888.

[6] *Ber.*, 44 (1911), 202.

[7] *Ann. chim. phys.*, [9] 4 (1915), 28.

[8] *Atti. accad. Lincei*, 21 (1912), I, 779.

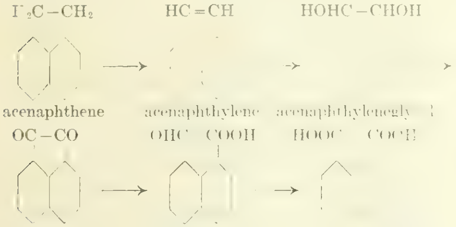
[9] Kalle and Co., D.R.P. 248,994 (1910).

Oxidation Products

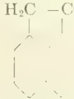
The most detailed work which has as yet been done in the field of acenaphthene chemistry has been concerned with a study of the products which are formed as a result of its oxidation. This has been due to the fact that the great majority of important commercial applications of acenaphthene deal with substances which are obtained by the action of various reagents upon acenaphthenequinone, acenaphthenone, or naphthalic acid, or upon some mixture of these and other derivatives which contain oxygen. The results of even the earliest studies in the oxidation of acenaphthene and its derivatives[1] showed conclusively that the products obtained as the result of any given reaction varied very considerably and that the yield of any single component of the reaction product depended very definitely upon the conditions.

It remained for C. Graebe in a series of brilliant investigations[2] to clear up the confusion which inevitably arose in regard to the relationships existing between acenaphthene and the various products which are formed as a result of its oxidation, and to establish the exact conditions under which the best yields of the more important of these products could be obtained. It is not within the scope of this paper to describe these processes in detail, but attention may properly be called to some of the conclusions which were arrived at as a result of this work.

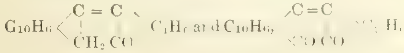
Reasoning from purely theoretical considerations the oxidation of acenaphthene may be assumed to proceed in the following stages:



Intermediate between acenaphthene and acenaphthenequinone, though deviating slightly from the straight course of oxidation indicated above, is still another substance which may also be regarded as a product of direct oxidation, namely, acenaphthenone.



All of these substances have been found actually to exist, although all have not been obtained by the direct action of oxidizing agents upon acenaphthene itself. In addition to these, still other compounds are known which may be assumed to represent secondary products of oxidation, and one of which at least has been shown to be present in all oxidizing mixtures. They are biacenaphthylidene ketone and biacenaphthylidene diketone, and may be assumed



$$C_{10}H_6\left\langle\begin{array}{c}C=C\\ |\\ CH_2\,CO\end{array}\right\rangle C_{10}H_6 \text{ and } C_{10}H_6\left\langle\begin{array}{c}C=C\\ \\ CO\,CO\end{array}\right\rangle C_{10}H_6,$$

to result from the condensation of one molecule of acenaphthenequinone with one molecule of acenaphthene or with one molecule of acenaphthenone, respectively.

The mixture which is actually formed by the action of oxidizing agents upon acenaphthene always contains a number if not all of these substances. The three which are practically always present and which are produced in relatively large quantities are acenaphthenequinone, naphthalic acid, and biacenaphthylidene diketone. Two others, acenaphthene and naphthaldehydic acid, have also been isolated in small quantities,[1] while the presence of acenaphthenone is at least indicated. The practical importance of acenaphthenequinone and naphthalic acid was immediately recognized, and the researches of Graebe had as their principle objective the determination of the exact conditions under which these substances were respectively formed. As a result of these experiments, methods were finally developed by means of which 40 per cent acenaphthenequinone and practically theoretical yields of naphthalic acid could be obtained by the direct action of reagents upon acenaphthene. These classical researches of Graebe represent such an exact and careful study that no reports as to modifications and improvements in method occur in any of the succeeding literature on the subject. It has in fact been found difficult always to realize fully the yields which are described in these experiments, and F. Ullman,[2] for example, states that although he has followed Graebe's procedure as closely as possible he has been unable to obtain yields above 40 per cent of naphthalic acid, although theoretical yields are claimed for the process. Graebe himself emphasizes the need of the most minute care in maintaining the very exact conditions which he describes during the entire course of the oxidation. He also emphasizes the need of great precision in handling the resulting mixture, since the exact concentrations of sodium hydroxide and sodium carbonate which are used at different stages in the separation seem to be of the utmost importance. If these reagents are used carelessly, or in other concentrations than those which are described, they may act to produce chemical changes in the substances whose separation is desired. For example, the separation of acenaphthenequinone depends upon its solution in aqueous sodium hydroxide. If the alkali is dilute (5 per cent) practically all of the quinone is precipitated unchanged upon the addition of mineral acid, while if the alkali is concentrated (30 to 35 per cent) the solution gives an almost quantitative yield of naphthaldehydic acid.

The history of the development of the chemistry of the oxidation products of acenaphthene followed the natural course. Separate methods for the preparation of acenaphthylene glycol, acenaphthenone, acenaphthenequinone, naphthaldehydic acid, and naphthalic acid were first studied and perfected, after which investigations in regard to the chemical reactions and important commercial applications of these respective compounds were undertaken. The latter portion of this paper will be devoted to a summary of the results which have been arrived at in each case to date, but before proceeding to the separate discussion of these different substances the fact may be noted that at least in one of their applications, namely in the field of dye chemistry, it is not always necessary to separate them individually from the mixtures in which they occur. Recent German patents cover the condensation of the crude products obtained by the direct oxidation of acenaphthene, with such substances as indoxyl, isatin, oxythionaphthene, and others which may be used in the preparation of red vat dyes. According to D. R. P. 236,536 of the Basler chemischen Fabrik, for example, the crude oxidation product from acenaphthene and sodium bichromate in acetic acid is treated in the presence of an amine with bisulfite in aqueous solution, when a substance which is assumed to be an arylido-bisulfite derivative of acenaphthenequinone separates from the solution in crystalline form.[1] This is then treated with 3-oxy-1-thionaphthene or the corresponding acid according to the method described in D.R.P. 196,016. In cases where the oxidation of acenaphthene is effected by the action of esters of nitrous acid such as ethyl and amyl nitrite,[2] the crude product, which contains along with other substances a compound having the composition of acenaphthenequinone monoxime, may be condensed in the presence of formic or oxalic acid with indoxyl, 3-oxy-1-thionaphthene, or their respective derivatives.[3] A supplement to this patent covers condensations in the presence of reducing agents other than formic and oxalic acid.[4] The significance of these facts will become more apparent after a more detailed study of the chemistry of the oxidation products of acenaphthene.

---

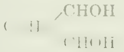
[1] Compare Behr and Van Dorp, *Ber.*, **6** (1873), 60; *Ann.*, **172** (1874), 263. M. Blumenthal, *Ber.*, **7** (1874), 1092; Quincke, *Ber.*, **20** (1887), 609; **21** (1888), 1454; Crompton, *Proc. Chem. Soc.*, **28** (1912), 194.

[2] *Ber.*, **20** (1887), 237, 657, **25** (1892), 652; *Ann.*, **276** (1893), 12; **290** (1896), **290** (1896), 195, 205; **327** (1903), 47.

[1] *Ber.*, **43** (1910), 440.

[2] *Ber.*, **43** (1910), 440.

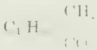
Acenaphthylene glycol,



$$C_{10}H_6\left\langle\begin{matrix}CHOH\\CHOH\end{matrix}\right.$$

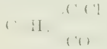
represents a product which has not as yet been obtained by the direct oxidation of acenaphthene. It has been prepared from acenaphthylene bromide (1) by first transforming the latter into its acetate and then saponifying the product,[1] and (2) by boiling the bromide with water.[2] In both instances the yields are relatively small, and for this reason the substance is at present of litle more than theoretical interest.

Acenaphthenone,



$$C_{10}H_6\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right.$$

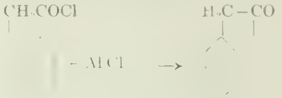
has been prepared from acenaphthylene glycol (1) by treating the substance with sodium alcoholate and methyl iodide,[3] and (2) by boiling for a few minutes with concentrated hydrochloric acid and then distilling with steam, when acenaphthenone appears in the distillate.[4] It has also been prepared by starting with acenaphthenequinone. In this case two methods of procedure are possible. The quinone may either be subjected to direct reduction in acetic acid solution by means of zinc dust, or it may be converted into its dichloride by treatment with phosphorus pentachloride and the product then reduced. Both methods give approximately the same yield (35 to 37 per cent of the acenaphthenequinone taking part in the reaction), but the second is the more convenient since less care is required in carrying out the experiment. The dichloro derivative of acenaphthenequinone



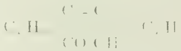
$$C_{10}H_6\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right.$$

which is formed as the intermediate product in this reaction is an interesting substance and its possibilities as a reagent in condensation reactions seem never to have been fully exploited.[1]

Still another method for the preparation of acenaphthenone involves the action of aluminium chloride upon α-naphthylacetyl chloride dissolved in nitrobenzene. The product is poured upon ice, and the acenaphthene is separated first by steam distillation and then by distillation under reduced pressure.[2] The reaction in this case may be expressed in terms of the following equation:



Acenaphthenone has been applied in a number of condensation reactions. It itself polymerizes in the presence of alcoholic alkali or acetyl chloride to give biacenaphthylidene ketone,



$$C_{10}H_6\left\langle\begin{matrix}C=C\\CO\ \ CH_2\end{matrix}\right\rangle C_{10}H_6$$

Acenaphthenone, or derivatives of acenaphthenone in which the hydrogen of the methylene group has not been replaced, gives indigoid dyes[3] when condensed with derivatives of isatin, or naphthisatin which contain an α-ketone oxygen atom. A supplement to D.R.P. 212,858 provides for the substitution of 2,3-diketo-dihydrothionaphthene in place of acenaphthenequinone in condensation reactions with acenaphthenone.[1] It should be noted that in addition to a reactive carbonyl group acenaphthenone possesses methylene hydrogen hich is very reactive. In view of this fact it seems rather remarkable that the literature dealing with the chemistry of this substance should be relatively so meager.

ACENAPHTHENEQUINONE—Acenaphthenequinone is always formed in the oxidation of acenaphthene. Neither the character of the oxidation medium nor the quantities in which it is used seem to influence the yield of acenaphthenequinone very materially, but, on the other hand, the speed with which the reaction is carried on appears to be of great importance. Even under the most favorable conditions, however, the yield of acenaphthenequinone does not exceed 40 per cent of theory. This is due at least in part to the fact that the substance itself is very reactive. In the presence of oxidizing agents, for example, it tends to undergo further oxidation, passing into naphthalic acid, and in the presence of alkali (employed to effect the separation of acenaphthenequinone in most of the earlier investigations) it may undergo a variety of transformations. To mention but two of many reactions which may result from the action of alkali, the substance may add one molecule of base to form a salt of naphthaldehydic acid or it may condense to give biacenaphthylidene-diketone. The device of precipitating the quinone in the form of its bisulfite addition product[2] or in the form of its monoxime[3] does not appear to have eliminated completely the difficulties presented in the preparation of this valuable and important compound. Methods of catalytic oxidation, involving as they do the immediate removal of the oxidation product from further action of the oxidizing medium, would seem to offer promising results but, so far as is indicated by any references in the literature, they have not as yet been applied to the solution of this particular problem.

---

[1] Compare Basler chemischen Fabrik, D.R.P. 205,377, and 211,696.

[2] Kalle and Company, D.R.P. 224,979 and 228,698 (1911); also Brit. Patent 19,340 and 19,341, also French Patent 419,379.

[3] Basler chemischen Fabrik, D.R.P. 232,714 (1911).

[4] Basler chemischen Fabrik, D.R.P. 233,473 (1911).

[5] T. Ewan and J. B. Cohen, *J. Chem. Soc.*, 55 (1889), [illegible]

[6] C. Graebe and J. Jequier, *Ann.*, **290** (1896), 205.

[7] T. Ewan and J. B. Cohen, *Loc. cit.*

[8] C. Graebe and J. Jequier, *Loc. cit.*

[9] Basler chemischen Fabrik, D.R.P. 210,813 (1909).

[1] Basler chemischen Fabrik, D.R.P. 230,237 (1909).

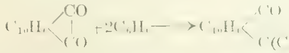
[2] Fr. Bayer and Co., D.R.P. 237,819 and 237,266.

[3] Basler chemischen Fabrik, D.R.P 226,244 (C.I.B.A.); French Patent 0,542; Compare D.R.P. 212,858 (C.I.B.A.); also D.R.P. 218,992 (B.A.S.F.),- French Patent [illegible]

[4] *Ann.*, **276** (1893), 7.

[5] A. Reissert, *Ber.*, **44** (1911), 1749. Compare Kalle and Co., D.R.P 224,979 and 228,698; Brit. Patent 19,340 and 19,341; French Patent 419,379; also Francesconi, *Gazz. chim. ital.*, **33** (1903), 42; and J. C. Cain, "The Manufacture of Intermediate Products and Dyes," p. 242, 1919, Macmilian Co.

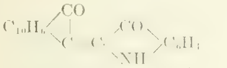
The literature dealing with the chemistry of acenaphthenequinone is very voluminous. It consists in large part of descriptions of condensation reactions which commonly involve one molecule of the quinone and one or more molecules of the different compounds which have been found to be capable of coupling with it. Some of these reactions, as for example, those which are brought about by the action of amino hydrogen and which result in the elimination of water, have already been considered in connection with a discussion of the properties of the amino derivatives of acenaphthene. Another general type of reaction takes place when acenaphthenequinone is condnsed with aromatic hydrocarbons or their derivatives in the presence of aluminium chloride.[1] In this case the oxygen of the carbonyl group reacts with ring hydrogen atoms, and the elimination of water is accompanied by the formation of substances which belong to the group of fluorescoin dyes:



$$C_{10}H_6{<}\begin{matrix}CO\\|\\CO\end{matrix} + 2C_6H_6 \longrightarrow C_{10}H_6{<}\begin{matrix}CO\\ \\C(C_6H_5)_2\end{matrix}$$

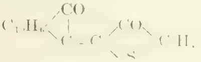
This reaction seems to be capable of as many different forms of application as are possible in the case of phthalic anhydride and other substances of this class. A third general type of condensation takes place as a result of the action of acenaphthenequinone upon compounds which contain halogen. Here the elimination of halogen acid is accompanied by the substitution of organic residues for one or both of the hydrogen atoms which occupy peri-positions to the carbonyl of the quinone. References to this type of reaction have already been considered in connection with the preparation of certain of the derivatives of acenaphthene and also in connection with the synthesis of the higher indandiones.

The fourth and most important general type of condensation reaction involves the preparation of vat dyes belonging to the class of indigoids. This particular phase of the chemistry of acenaphthenequinone is of great commercial importance. The literature is voluminous and includes a large number of German patents. This field of work was opened up as a result of the discovery, made more or less simultaneously in 1908 by A. Bezdrik coöerating with P. Friedlander[2] and by A. Grob,[3] that the oxygen of the carbonyl groups in acenaphthenequinone is capable of entering into condensation reactions with indoxyl and with oxythionaphthene to form products which are analogous to indigo and which possess the following unsymmetrical formulas:



$$C_{10}H_6{<}\begin{matrix}CO\\|\\C\end{matrix}{=}C{<}\begin{matrix}CO\\NH\end{matrix}{>}C_6H_4$$

and acenaphthene-indol-indigo



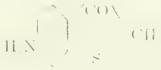
$$C_{10}H_6{<}\begin{matrix}CO\\|\\C\end{matrix}{=}C{<}\begin{matrix}CO\\S\end{matrix}{>}C_6H_4$$

acenaphthene-thionaphthene-indigo

The second of these two substances represents a valuable sulfur vat dye and is known commercially under a number of different names, *viz.*, Ciba Scarlet G (B.A.S.F.). Thioindigo Scarlet 2G (Kalle and Co.), Helidone Scarlet C (M.L.B.).

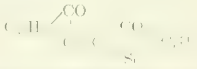
The original patents[4] which covered the preparation of the parent substances were quickly supplemented by others which describe their bromination,[1] the dye obtained from Ciba Scarlet G, for example, being known under the trade name of Ciba Red R. Later patents describe the formation of halogenated red vat dyes which are formed under a variety of different conditions.[2] These are so phrased as to cover all halogenated products which may be regarded as derived from acenaphthenequinone, its homologs, and substances analogous to it.

Succeeding patents describe the behavior of acenaphthenequinone in the presence of various *derivatives* of indoxyl and oxythionaphthene respectively.[3] Ciba Orange G represents, for example, a substance which is obtained by brominating the condensation product from acenaphthenequinone and 6-amino-3-oxythionaphthene,



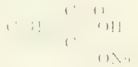
A gray-black vat dye[4] is prepared by condensing 5-amino-3-oxythionaphthene with acenaphthenequinone, and coupling this compound with that obtained by condensing 6-amino-3-oxythionaphthene with acenaphthenequinone. Bromination of the product is included in certain instances. The scope of this work has gradually broadened and has come to include reactions between acenaphthenequinone and a large number of different organic compounds such as, for example, B-naphthindoxyl,[5] phenyl-thioglycol-o-carboxylic acid,[6] etc. Indeed the patent literature on this subject is frequently very difficult to follow, since the specifications which cover the condensations of acenaphthenequinone and its derivatives with derivatives of indoxyl, oxythionaphthene, and similar substances are phrased in such general terms that they may be said to include all the reactions which are possible between carbonyl oxygen, present in every variety of α-diketone grouping, and reactive methylene or methine hydrogen present in any form of combination.[7]

Other indigoids are theoretically possible and acenaphthene-selenonaphthneindigo, for example,



has been prepared and described by L. R. Lester and R. Weiss.[8] This appears, however, to be a substance of no commercial importance.

Kalle and Company suggest the treatment of acenaphthene quinone with caustic alkali prior to condensation, since a water-soluble body,



has been observed to form as a result of this action. This yields vat dyes when condensed with 3-oxythionaphthene, etc.[9] The same firm also describes the treatment of acenaphthenequinone with mild reducing agents when the following transformations occur:

---

[1] Compare M. Zsuffa, *Ber.*, 43 (1910), 2915.

[2] *Monatsch.*, 29 (1908), 359.

[3] *Ber.*, 41 (1908), 3331.

[4] D.R.P. 206,647 and 205,377 (B.A.S.F.).

[1] Compare D.R.P. 198,510 and 196,349 (B.A.S.F.) respectively.

[2] D.R.P. 213,504, 212,870, 237,199, 237,266, 241,825, 241,826, 241,827; also Brit. Patent 3730.

[3] D.R.P. 234,178 (Fr. Bayer and Co.).

[4] D.R.P. 258,099 (M.L.B.).

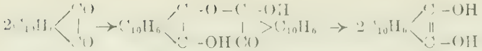
[5] D.R.P. 235,811 (M.L.B.).

[6] D.R.P. 205,377 (B.A.S.F.).

[7] D.R.P. 209,910, Kalle and Co., 1909.

[8] *Ber.*, 45 (1912), 1835.

[9] Compare D.R.P. 209,910, 243,536, 246,338 (Kalle and Co.).

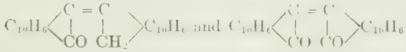


$$2C_{10}H_6\left\langle\begin{matrix}CO\\|\\CO\end{matrix}\right. \rightarrow C_{10}H_6\left\langle\begin{matrix}C-O-C-OH\\|\qquad\quad|\\C-OH\;CO\end{matrix}\right\rangle C_{10}H_6 \rightarrow 2C_{10}H_6\left\langle\begin{matrix}C-OH\\\|\\C-OH\end{matrix}\right.$$

The last compound is capable of condensing with indoxyl or with 3-oxynaphthene to form violet or violet red vat dyes.[1] Both modes of treatment of acenaphthenequinone are covered by French patents[2] which include the preparation of all derivatives of the above dyes which can be obtained by brominating, diazotizing, etc.

In conclusion it should be noted that many of the reactions described in these patents have not been applied since the use of simple derivatives of acenaphthenequinone in the various types of condensations has been prevented by the fact that very few of these compounds are as yet actually known.

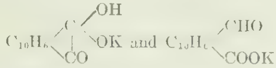
OTHER OXIDATION PRODUCTS—In continuing the systematic survey of the chemistry of the oxidation products of acenaphthene it must be confessed that very little of importance remains to be said. Biacenaphthylidene ketone and biacenaphthylidene diketone,



$$C_{10}H_6\left\langle\begin{matrix}C=C\\|\quad\;\;|\\CO\;CH_2\end{matrix}\right\rangle C_{10}H_6 \text{ and } C_{10}H_6\left\langle\begin{matrix}C=C\\|\quad\;|\\CO\;CO\end{matrix}\right\rangle C_{10}H_6$$

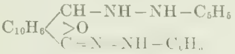
represent secondary products formed by the action of various reagents upon acenaphthenone and acenaphthenequinone. Both compounds were investigated by Graebe and have already been referred to.

Naphthaldehydic acid is an interesting substance, the salts of which seem to exist in two tautomeric modifications, *viz.*,



$$C_{10}H_6\left\langle\begin{matrix}C\overset{OH}{\diagup}\\|\;\;\diagdown OK\\CO\end{matrix}\right. \text{ and } C_{10}H_6\left\langle\begin{matrix}CHO\\COOK\end{matrix}\right.$$

It is formed when acenaphthenequinone is dissolved in aqueous potassium hydroxide (30 to 33 per cent). The free organic acid is precipitated by mineral acids and purified by crystallization from dilute alcohol. The yield is almost quantitative.[3] Naphthaldehydic acid condenses with phenylhydrazine to give



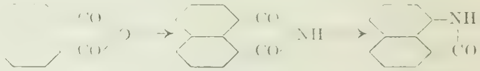
$$C_{10}H_6\left\langle\begin{matrix}CH-NH-NH-C_6H_5\\>O\\C=N-NH-C_6H_5\end{matrix}\right.$$

Its condensation products with acetone and acetophenone have been investigated by J. Zink,[5] and those with methyl-*m*-tolyl ketone and pinacoline by S. Wiechowski.[6] Patents based upon the formation of naphthaldehydic acid from acenaphthenequinone have already been referred to.[7]

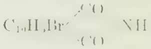
The oxidation of acenaphthene to naphthalic acid or its anhydride was studied by all of the earlier investigators in the field of acenaphthene chemistry.[8] The process in every instance involved the use of sodium or potassium bichromate and sulfuric acid, but the yield seems to have varied very considerably. Behr and van Dorp obtained yields of 16 to 20 per cent, while Graebe was able to secure results which he described as almost quantitative. F. Ullmann[9] was, however, unable to increase his yields above 40 per cent even by using sodium bichromate and following Graebe's procedure very exactly. The difficulty seems to be that of carrying the reaction far enough to avoid the presence of the lower oxidation products of acenaphthene and yet stopping it before any appreciable quantities of naphthalic acid have been decomposed. It may be noted in this connection that the ease with which peri-derivatives of naphthalene undergo oxidation is very great.[1]

As its name shows, the similarity in the behavior of naphthalic and phthalic acids was recognized at an early date.[2] The fact that the resemblance between the two substances is very close and very striking might be assumed to indicate the possibility of a large number of important applications for naphthalic acid. For example, the very valuable but somewhat incomplete collection of names and references to derivatives of phthalic anhydride which has been compiled by Dr. Max Phillips of the Color Laboratory, Bureau of Chemistry, Washington, D. C.,[3] suggests many interesting lines of investigation which might be undertaken in connection with a more extended study of the chemistry of the anhydride of naphthalene-peri-dicarboxylic acid. Very little work has as yet been done in this field. The action of naphthalic anhydride upon dimethyl-*m*-aminophenol has been the subject of investigation by E. Ferrario and L. F. Weber,[4] but aside from this no references to direct condensations have been noted in the literature.

A number of derivatives of naphthalic anhydride have been described. F. Ullmann and E. Cassirer[5] have succeeded in preparing naphthostyril by means of the following transformations:

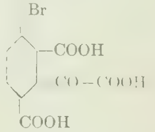


Among the other derivatives which have been investigated are chloronaphthalic acid,[9] bromonaphthalic acid and the corresponding iodide,[7] 4-nitronaphthalic acid and the cor-



$$C_{10}H_5Br\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$$

responding imide,[8] 4-aminaphthalic acid, 4-hydroxynaphthalic acid, 3-nitronaphthalic anhydride, and 3-aminonaphthalic anhydride.[9] The oxidation of 4-bromonaphthalic acid to bromophenylglyoxyldicarbonic acid



has also been described.[10]

In conclusion it may again be stated that the footnotes which accompany the foregoing synopsis represent all of the references to the chemistry of acenaphthene and its derivatives which can be obtained by a fairly close and systematic study of the literature. The discussion has been as detailed as it has seemed practical to make it in the hope that the material presented might prove of actual service as a basis for further research in this field.

---

[1] D.R.P. 22[illegible],158, 221,979, also U. S. Patent [illegible]70 and Brit. Pat. 21,579.

[2] French Patent 407,224, 407,225, 407,226, 407,227, 407.228.

[3] *Ann.*, **290** (1896), 202; *Ber.*, **25** (1892, 657; *Ann.*, **276** (1893), 18

[4] *Ann.*, 276 (1893), **14**.

[5] *Monatsh.*, 22 (1901), 8[illegible]

[6] *Monatsh.*, **26** (1905), 749.

[7] D.R.P. 243,536 (Kalle and Co.).

[8] Behr. and W. A. van Dorp, *Ber.*, **6** (1873, 60; *Ann.*, **172** (1874), 263; E. Bamberger and M. Philipp, *Ber*, **20** (1887), 237; C. Graebe, *Ber.*, **20** (1887), 657; **25** (1892), 652; T. Ewan and J. B. Cohen, *J. Chem, Soc.*, **55** (1889), 578.

[9] Ber., **43** (1910), 440.

[1] Compare G. Errera and G. Ajon, *Gazz. chim. ital.*, **44** (1914), II, 9[illegible]

[2] A. Behr and W. A. van Dorp, *Loc. cit.*

[3] THIS JOURNAL, **13** (1921), 247.

[4] *Arch. sci. phys. nat.*, **25** (1908), 517.

[5] *Ber.*, **43** (1910). 439; Cpomare C. Graebe, *Ber.*, **35** (1902), **44**.

[6] H. Crompton and W. R. Smythe, *Proc. Chem. Soc.*, **25** (1912), **194**.

[7] Blumenthal, *Ber.*, **7** (1874), 1092; Graebe, *Ann.*, **327** (1903), **86**.

[8] Quincke, *Ber.*, **21** (1888), 1455; Graebe, *Ann.*, **327** (1903), 82.

[9] See Graebe, *Loc. cit.*

[10] *Ann.*, **327** (1903), 90.

European Practice in Cellulose Acetate and Dopes During the War [1, 2]

By Philip Drinker

Laboratory of Applied Physiology, Harvard Medical School, Boston, Massachusetts

Although many substances have been suggested and many formulas developed for the coating and preservation of airplane fabrics, with the exception of the relatively noninflammable cellulose esters typified by the cellulose acetates, none have received governmental recognition for any extended period of time. In this connection, the cellulose nitrates have received but minor consideration, primarily on account of their greater inflammability, combined with the fact that they do not exhibit properties other than those shown by the corresponding acetic esters.

An historical account of the development of airplane dopes necessarily involves an account, first, of the trial and rejection of cellulose ester substitutes, and secondly, of the improvement of the many combinations and modifications in which cellulose acetate enters as the primarily solid constituent. So far as the writer is aware, the most complete and comprehensive data on the general subject of airplane dopes and cellulose acetate thermoplastic combinations are contained in a 1050-sheet typewritten *Report* **10,086** of E. C. Worden, made in 1918, and the 5040-sheet typewritten *Report* **13,228**, with index, of E. C. Worden, Philip Drinker, J. S. Buford, Leo Rutstein, and R. G. Dort,* made in 1919, to the Bureau of Aircraft Production in Washington—reports embodying the results of extended investigations made by the writers abroad and in the United States. Many of the facts and figures incorporated in this article have been abstracted from these reports.

In Europe, at least, the term *dope* was in use in 1914[2] as indicating the nitrocellulose and cellulose acetate solutions which are applied to airplane fabrics to impart increased tensile strength, tautness, and resilience, and to increase impermeability. Present practice requires the several coatings to give a total weight increase to the fabric of approximately 2 ounces per square yard (60 to 70 grams per square meter), and to retain their protective beneficial qualities on exposure to atmospheric weathering conditions, usually for periods of 60 to 90 days. These specifications are the outgrowth of experience during the war, at the commencement of which requirements were less rigorous.

An account of the various French dopes has been given by M. Deschiens,[3] who records the use of nitrocellulose coating, in 1896, on a balloon destined for polar exploration. In this case the dope was purely for protection and not for tautening effects. Substitutes such as casein, glue, gelatin, starch pastes, rubber, etc., have been tried at various times, in both England and France, but their use has never passed beyond the experimental stage, and, at the outbreak of the war, the use of nitrocellulose and cellulose acetate dopes was firmly established in Europe and existed to a certain extent in the United States. As a result of its greater inflammability, the nitrocellulose product was soon rejected by the French, while, as the war progressed, the British program called for a like procedure when adequate supplies of cellulose acetate were available. Marked preference was also shown by the Italians for cellulose acetate dopes. The example of the other Allies was later followed by the United States, the American program calling for all planes destined for the front to be coated with acetate dopes, nitro dopes being limited to training planes. This procedure was identical with that of the British.

Commercial Development of Cellulose Acetate

Prior to the summer of 1914, cellulose acetate was manufactured in commercially interesting quantities by only three European firms, *viz.;* the Bayer Company at Leverkusen, the Société Chimique des Usines du Rhône at Lyons, and the Cellonite Company (Dreyfus Bros.) at Basle. Bayer acetate was used by certain British firms and is reliably reported as being satisfactory, while that furnished by the French company was also received with favor. In France the Usines du Rhône product was in general use, so that the outbreak of hostilities found the British depending for their supply on their French Allies and on the product of a neutral country, no adequate supply of German acetate having been accumulated.

As the war progressed and their aircraft program augmented, the French required more and more of their own product, with the result that shipments to Great Britain were reduced to a minimum. The British program called for an amount of acetate soon evident to be far in excess of the assured supply, coming as it did from outside sources. This state of affairs resulted in negotiations with the Dreyfus Bros.[4] whereby the erection of a large plant for the manufacture of cellulose acetate was undertaken at Sponden, England. This plant also included a synthetic acetic acid and acetic anhydride unit. To assure further their own supply, a similar but smaller Dreyfus plant was built by the French at Rouen, while plans for a Dreyfus plant at Milan were laid down by the Italians. This example was later followed by the United States at Cumberland, Md. Throughout the war, the French used the Usines du Rhône product in greater part—a product characterized by its uniformity in the chemical and physical qualities essential for dopes. With the completion of the Dreyfus English plant, British dopes were made almost solely from this latter source of acetate, a state of affairs prevailing at the close of the war when a standard dope formula, obligatory for all manufacturers, had been developed. That the Dreyfuss acetate successfully met the specifications for this standard dope over an extended period is sufficient proof of its uniformity.

The cellulose acetate resources of Germany have been said to be greater than those of the Allies. The acetate of the Bayer Company has already been mentioned as one of the three types produced in Europe at the outbreak of the war. Personal visits by E. C. Worden[5] and the writer,[6] on behalf of the Bureau of Aircraft Production, to a small plant at Mainz showed an additional source which is known to have been utilized by the Germans during the war. Samples of gelatin-coated gas-mask eye pieces, made of cellulose acetate, from the Aktiengesellschaft für Anilin Fabrikation were also observed from time to time. Fabrics from German and Austrian planes invariably showed cellulose acetate dope, and, knowing their plant resources, it is but reasonable to presume they had no special difficulties in meeting requirements, although no reliable data are available to us on their cellulose acetate output. All the plants known to have been engaged in its production were located far from the front, and evidences of destruction of

---

[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published by permission of the Chief of Air Service, U. S. Army.

* Number in text refer to Bibliography at end of paper.

their chemical factories by Allied aircraft were not apparent. In fact, the general atmosphere of the enemy chemical plants, as disclosed from visits to their factories in the occupied region, was decidedly one of prosperity and preparedness for the future.

CHEMICAL CHARACTERISTICS OF CELLULOSE ACETATE

Of the many variations in processes used for the production of cellulose acetate all employ the same basic principles, *viz.;* acetylation of cellulose by glacial acetic acid and acetic anhydride in the presence of a catalyst such as sulfuric acid. The Dreyfus processes[7] involve the use of paper as the preferred source of cellulose, while it is understood that the Société Chimique des Usines du Rhône employs a long-staple cotton, previously treated. For airplane dope, in both cases the objective is an acetone-soluble acetate, between the diacetate and triacetate in acetic content, which is attained by acetylation temperature control and the subsequent ripening process. In an exhaustive study of the subject, E. C. Worden[9] has traced the development of cellulose acetate from the carbohydrate acetylations of Schützenberger through to the modern period, and has pointed out the importance of the Dreyfus discoveries in the development of this art. In this article, he shows that the acetates preferred for photograph films and artificial filaments differ fundamentally from the product used for dopes, the former demanding clarity as an essential characteristic, while the latter must possess relatively greater tensile strength, clarity of the dope film being of less importance. Primary acetates, possessing acetone solubility as a permanent characteristic, and having passed through the chloroform-soluble stage, are among the qualities necessary for dopes in which chlorinated solvents do not enter. H. Ost,[10] C. Cross and E. Bevan,[11] and G. J. Esselen, Jr.[12] have contributed to the literature on this subject, the last author discussing the colloidal nature of the cellulose acetate molecule and distinguishing the chloroform and acetone-soluble acetates by the solvents which may be employed.

Of the Usines du Rhône and Dreyfus products, the former generally possessed the more rapid acetone solubility, due perhaps to finer state of mechanical division of the particles. Dreyfus aimed to produce an acetate of relatively higher viscosity[13] which could be applied in a three-coat doping scheme, and which would give a film of tensile strength equal to that formerly attained by applying as many as six coats. This resulted in a substantial solvent economy so imperative in the successful prosecution of the British aircraft program.

SOLVENTS, DILUENTS, PLASTICIZERS, AND PIGMENTS

The selection of solvents and solvent combinations was determined by each country primarily from the resources available, a condition which prevailed throughout the war, and which underwent a gradual development resulting in the ultimate adoption of standard formulas. Since over fifty different solvent combinations—a number of them secret—emanating from the Allied governments and from firms supplying dope, were suggested and used at one time or another, a detailed historical account would be inexpedient. The subject can well be covered in a review of the essential points of difference of the various combinations, as their use developed during the course of the war. The use of tetrachloroethane as a solvent was prohibited by France, and later by Great Britain, because of its toxicity and tendency towards decomposition, as result of which the fabric was materially weakened. Actual fatalities[14] were traced to the toxicity of this solvent. The work of W. Willcox, B. Spillsbury, and T. Legge[15] showed that a characteristic type of toxic jaundice, affecting the liver, developed from inhaling tetrachloroethane fumes. Both countries, and Italy as well, prohibited the use of chlorine substitution products, an example followed later by the United States. Consequent to these discoveries, the British enforced rigid ventilation of their doping shops and required at least thirty changes of air per hour.

Somewhat before our entry into the war, the French were using a four-coat dope designed for purposes of camouflage, which at that time was considered by them to be indispensable. A typical French dope, patented under the trade name of *Acellos* by Nauton Frères et de Marsac, the patentee being their chemist, T. Tesse,[16] was in special favor, while L. Clement and C. Rivière[17] produced a somewhat similar product. In *Acellos* dope the scratch coat contained 3 to 5 per cent acetate and was low in high boiling solvents, by which means greater tautening effects were said to be produced. The second and third coats required 8 to 9 per cent acetate and about 2 per cent of mineral or metallic pigments, the vehicle for which was usually eugenol, while other high boilers and plasticizers, such as benzyl alcohol, triacetin, isoeugenol, carvacrol, safrol, isosafrol, methyleugenol, and glyceryl benzoate, could be employed. The fourth and final coat required about 8 per cent acetate, while the high boilers were again cut down. The under surfaces of the planes received second and third coats of aluminium color and upper surfaces were given a variegated camouflage scheme intended to resemble the earth's surface. Planes used in night flying were colored dark, the dopes being applied exactly as were those for the day planes. None of the French planes destined for the front received a varnish coating of either oil or nitrocellulose base. This treatment was claimed to impart special characteristics of tautness and to increase invisibility of the plane from both above and below, an idea which gradually lost favor until, at the end of the war, the French followed the British example and adopted colorless dopes with a finishing coat of khaki color on upper surfaces.

British practice went through a similar but seemingly more logically coördinated and technically controlled development. While the French relied mainly on methyl acetate of local manufacture for their low boiling solvent, the British had recourse principally to acetone, furnished in large part by the United States and Canada. In a general report, J. Ramsbottom[2] discusses cellulose acetate solvents and points out the latent solvent effects of a mixture of benzene and alcohol, each of which in itself is a non-solvent at ordinary temperatures, a point mentioned later by G. J. Esselen, Jr.[18] Efforts to obtain a satisfactory three-coat standard formula requiring the maximum amounts of the non-pyroligneous products, ethyl alcohol and benzene, resulted in 1918 in a British formula[19] in which acetone, methyl acetate, ethyl formate, or methylethylketone could be used as the low boiling solvents, alcohol and benzene as the diluents, benzyl alcohol as high boiler, and triacetin and triphenyl phosphate as softeners.[20]

To these lists the French added a locally manufactured low boiling product, known as *C.G.H.*, which consisted in a mixture of approximately 70 per cent methyl acetate, 16 per cent acetone, 12 per cent methyl alcohol, and 2 per cent water. In addition to the high boiling solvents already mentioned, the French suggested acetoacetic ester and furfurol, and towards the end of the war, amyl and isobutyl alcohol,[21] of which a French firm offered a considerable supply. Dechitns[3] mentions their having investigated in addition the following substances: methyl, ethyl, amyl, and butyl lactates and oxalates, glycol diacetin, benzylidene diacetate, diphenyltolyurea, and cresol,[22] none of which passed beyond experimental stages. Cyclohexanol and cyclohexanone[23] were also suggested from both British and French sources, but were never used in any quantity, although said to be efficient. Acetic and formic acids were used experimentally as solvents and did not appear to weaken the fabric materially.[24]

Unlike the British, the French dopes contained no solid softeners such as triphenyl phosphate, although the French had attempted using both this and tricresyl phosphate, principally as fire retardants.[25]

Having adequate supplies of phenol, the Italians generally used a small percentage of this substance—2 to 3 per cent, depending on the type of fabric for which the dope was destined. Their formulas, like several of the French ones, were varied somewhat in winter and summer to compensate for rapidity of solvent evaporation. The Italians permitted a certain latitude in the choice of low boiling solvent combinations and also used no tricresyl or triphenyl phosphates.

The United States developed a standard four-coat scheme in which the scratch coat contained a small percentage of phenol and napthalene, and, as antacid, a small percentage of urea or dicyanodiamide. For the three subsequent coats, there was included in the formula about 7 per cent of diacetone alcohol, principally to prevent blushing, with small amounts of benzyl acetate and benzoate. The United States' formula embraces the greatest number of ingredients, but it must be remembered that this formula was based on supply and economy in local resources.

German and Austrian Practice

Critical periodic examinations of enemy fabric obtained from captured or destroyed aircraft, both lighter- and heavier-than-air, disclosed a few important points differentiating their fabric and dope from those of the Allies. The enemy planes were frequently camouflaged in multicolored dyes, printed on the fabric in polygonal designs. The airplane fabric was usually linen, showing evidences of heavy calendering, with a thread count averaging about 55 to 65 per inch for the warp and 45 to 55 in the weft. The tensile strength gave average minimum figures of 70 to 80 pounds per linear inch in the warp and 65 to 75 pounds in the weft, but it must be remembered that these figures are taken from used fabrics which had undoubtedly deteriorated to an appreciable extent, so that the tensile strength figures are probably low.

In most instances the doped fabrics were covered with an alcohol-soluble varnish, colorless or pigmented, showing a dry weight increase due to the varnish of anything from 0.5 to 2 ounces per square yard. The dope films were of notably less weight than those used by the Allies and were in the neighborhood of 1 to 1.5 ounces per square yard. Comparative analyses of scrap Allied fabric showed at least 2 ounces of dope film per square yard and frequently more. A few German fabrics showed evidences of chlorinated compounds as cellulose acetate softeners, but extraneous matter was, in general, not found to be present.

Methods of Applying Dopes

Since the major percentage of ingredients of both cellulose acetate and nitrocellulose dopes is made up of low boiling hygroscopic liquids, their evaporation is rapid, an effect in some measure retarded by the addition of softeners and high boiling solvents. In both types of dope the cellulose ester can readily be precipitated by the addition of water, which explains the formation of the *white spots* or *blushing* so familiar on fabrics doped in damp and exceptionally drafty doping shops. Directions by the manufacturers and by all the governments required the dopes to be applied to dry fabric, while the United States alone enforced any attempt at humidity control, the European Allies merely suggesting its advisability.

Great Britain and the United States both required special brushes, approximately 4 inches wide with 2-inch bristles firmly fixed in the stock, a special brush wash being supplied in which the brushes were kept when not in use. Special cans were provided by Great Britain and the United States, these being designed to hold a conveniently portable quantity of dope of which a minimum of surface was exposed. Towards the end of the war a British firm developed a type of brush, through the handle of which dope was fed by air pressure, the dope being contained in a standard 10-gallon (Imperial) can. This brush, however, received no general usage. Both British and French made it a practice to save the skins or films which formed on the edges of the dope cans, these films being furnished to the manufacturers, who again used them, with judicious blending, in making up fresh dope.

Cellulose acetate doped fabrics, unprotected by a varnish coating, temporarily lose their tautness on becoming soaked, the tautness again becoming normal on the fabric's drying. This effect was most noticeable on French planes doped according to their four-coat scheme which required no varnish and no solid softeners. H. Gault[26] and the writer have taken advantage of this in a patent application for a process in which fabric, both linen and cotton, is mechanically coated with a cellulose acetate dope by spreading machine, for example, on both surfaces. When a wing or other member is to be covered the doped fabric is soaked in water and applied, moist, to the frame. When dried and varnished the fabric attains the required degree of tautness, while at the same time other properties conferred by dopes applied in the conventional manner are claimed to be equaled. The signing of the armistice prevented further investigations as to the value of this process, although laboratory and large-scale tests gave every indication that it had decided practical commercial possibilities for aircraft and possibly for other industries.

Great Britain and the United States very generally applied varnish covers and the colors for the insignia or identification marks by air brush. This method of application can be used for oil or nitrocellulose varnishes with equal facility, but no cellulose acetate dope which could be sprayed was developed, although a certain amount of experimental work was done.[27]

Effect of Sunlight on Doped Fabrics

It has been shown how important a factor was the question of supply in determining the various dopes used by the Allies; no less important was this same factor in standardizing the types of fabric. In place of line the United States gave precedence to a mercerized cotton of the type developed through the investigations of the Bureau of Standards, notably by E. Walen.[28] This cotton fabric fulfilled the specifications of the Allied countries, although its general acceptance and recognition was slow. In England linen made from Irish flax was preferred although cotton had fairly general acceptance, while France used linen, cotton, and silk. From her own resources Italy obtained silk, and both France and Italy, purely from economic reasons, used considerable quantities of this fabric in spite of its high cost.

It has been stated that both France and Great Britain abandoned the use of tetrachloroethane as a cellulose acetate solvent in dopes because of its toxicity and tendency to decompose. The cause of this decomposition was frequently ascribed to sunlight, although investigations at the beginning of the war do not appear to have been carried out to prove this point. The fact that both nitro and acetate doped fabrics gradually deteriorated, with a consequent loss in impermeability and tensile strength, was well recognized, but no means of retardation by agents, other than varnish, appears to have been attempted.

During 1918, F. Aston, at the Royal Aircraft Establishment, England, showed that the destructive action of sunlight on fabric, not the dope film, was principally due to ultraviolet light of wave lengths lying between 2950 and 4000 μ, and that the effect of these rays could be diminished by interposing an impervious layer or pigmented film. After testing various media, Aston showed that their coating, *P.C.* 10,[29] effectively impeded the destructive action of sunlight. This particular varnish has a base of nitrocellulose and khaki colored pigments of yellow ocher and lamp black, rendered plastic in a vehicle of castor oil. One coat of this varnish was applied by hand or air brush on upper surfaces of British planes. Following Aston's work, it was shown by others, notably the French, that the action of sunlight was more serious on silk than on cotton or linen, a point of interest to the Italians and French.[30]

A three-coat pigmented dope[31] was suggested by the British for Handley-Page night bombers, the resultant color scheme being much like that already in use by them at the time, except that under surfaces were also colored. The formula used for these pigmented dopes was very close to their standard and differed from the French colored dopes principally in the use of triphenyl phosphate, of which the British made much point. Although the British pigmented dopes showed considerable promise, they had received but limited application at the signing of the armistice.

SOLVENT RECOVERY

Solvents lost in the doping of aircraft fabrics were relatively small, compared with the solvents used in the manufacture of nitrocellulose powder, and it was quite natural that their recovery was of secondary importance in the question of solvent economy. By the centralization of plants engaged in covering and doping airplane parts, solvent recovery was in a fair way towards practical realization at the close of the war, so that a brief account will be given of two processes used in Europe.

L. Clement and C. Rivière attempted recovery by scrubbing the solvent vapors in cold water, a small plant for this purpose being built near Paris. The airplane wings were placed in horizontal troughs, of convenient height for the workers to dope, and the solvent vapors were drawn by fan down through a pipe running along the floor and thence to a scrubbing tower where the vapors met a descending shower of cold water, contact surface being furnished by coke. A number of doping troughs were connected in parallel to the vapor pipe, each trough having a damper for connecting into the system. Rolling curtains were placed across the end of each, and as doping progressed one curtain was rolled up and the other unrolled, thus affording a slight degree of control on the solvent content of the air entering the scrubber. The aqueous solutions at the bottom of the scrubber contained approximately 2 to 3 per cent of recoverable solvents with a total yield of about 30 per cent. The solvents captured were necessarily limited to the water-soluble, although the solubility of such substances as benzene, ordinarily water-insoluble, is enhanced by the presence of benzene solvents which in themselves are water-soluble. It is understood that the inventors claimed better yields could be effected, but no evidence available to the writer shows that this was accomplished on a scale of commercial interest.

For the recovery of ether-alcohol in the gelatinization and drying of nitrocellulose powder, the process of J. Bregeat,[33] which utilizes cresol, received extensive application during the war. It had been shown that certain phenolic bodies formed addition products with solvents such as acetone[34] which could be liberated on heating, the complex dissociating into its original components. Bregeat used this basic principle in attempting a substitute for sulfuric acid as an agent for ether-alcohol recovery, and first suggested the sulfonic acid of benzene but later found that cresol alone served as well and, in addition, was cheap and available in large quantities. The inventor claims the possible recovery of a number of volatile solvents, among which are the methyl, ethyl, and amyl alcohols and acetates acetone, benzene, toluene, xylene, and chloroform, from which it will be seen that the process is of interest in the cellulose acetate industries. Yields of 75 per cent of the solvents entering the system are guaranteed, while 92 per cent yields are said actually to have been obtained, figures which are supported by M. Deschiens.[32]

The success of his French plants, notably at Ripault, Sevran-Livry, and Toulouse, was such that Bregeat's process was recognized in Italy and England, where plants were built for ether-alcohol recovery. At H. M. Factory, Gretna, England,[35] sulfuric acid[36] had been abandoned and an experimental cresol plant installed, independent of Bregeat's engineering supervision. This plant proved so successful that a larger unit was undertaken, but was not finished until the close of the war.

The plants built by Bregeat usually include three scrubbing towers in which a large contact surface is obtained by a system of horizontal lattices of wood, scrubbing taking place on the countercurrent principle. At Gretna, rotary scrubbers made by the Whessoe Foundry Company were used, these being built up in twelve compartments giving a twelve-stage absorption. Contact surface was obtained by V-shaped wooden sectors, about one-quarter of an inch in thickness and sufficiently close together to pick up a film of cresol through which the solvent vapor passed as the scrubber slowly rotated.

For the liberation of ether-alcohol from cresol, Bregeat usually employs heat alone, while at Gretna live steam was considered essential. In either case the distilled solvents are subsequently rectified, while the cresol is returned to the scrubbers.

It has been shown in aircraft manufacturing that the weight decrease of freshly doped fabric proceeds at a fairly uniform rate for the first 15 to 20 minutes, after which solvent evaporation rapidly falls off. Tests, with cresol as the absorbent and using the standard British dope (D.100 specification), showed a yield of 50 to 60 per cent, with reliable indications that this would be exceeded in large-scale operations. Whether the fabric be doped in a vertical position from both sides at once or horizontally, is of no moment as regards the effect of the dope, but the former method is more rapid and will therefore give greater concentration of the solvent vapors in the air passing to the scrubbers. Vertical doping was adopted by the Voisin Company in whose aircraft works, near Paris, a Bregeat recovery plant was completed at the signing of the armistice. With locally devised improvements in the doping cabinets, all such modifications having as an objective the increased solvent concentration entering the scrubbers, this plant possessed the equipment then believed the best obtainable and endorsed by the Allied services.

Recovery of Cellulose Acetate From Scrap Airplane Fabric

To alleviate its shortage, investigations were undertaken both by independent firms and by the Allied governments towards the recovery of cellulose acetate from discarded airplane fabric, with the object of its resolution as such or mixed in part with fresh acetate. Mention has been made of the fact that the French used only cellulose acetate dopes on all planes, while the British used nitrocellulose dopes on training planes and finished off the combat planes with a nitrocellulose varnish for protection against ultraviolet light. Of the two systems, the French afforded the better opportunity for cellulose acetate recovery, inasmuch as the British required the separation of the two esters.

Of the several recovery processes suggested, all operated on the extraction principle and differed only in the choice of solvents and in certain details of mechanical manipulation. The Société Generale du Coton Industriel[21] suggested the use of cresol or furfurol as solvents, but it is understood that the former alone was used. This process requires extraction at temperatures in the neighborhood of 40° C., filtration of suspended mineral pigments, and precipitation of the cellulose acetate by benzene, followed by its purification with steam under reduced pressure, by which means it is claimed the acetate is not injured. The acetate thus recovered is undoubtedly degraded to a certain extent, but it is claimed to be satisfactory for dopes when mixed with fresh acetate.

J. Lumsden and R. Mackensie[33] proposed the use of solvents such as acetone for extracting the cellulose acetate. In one sense this would be an improvement over cresol, as the acetate need not be precipitated from solution but fresh dope could be made up with this as a basis.

Other solvents suggested were nitrobenzene, mixtures of methyl and ethyl alcohols and acetates, and tetrachloroethane. None of these methods were investigated on a scale of commercial interest over any extended period, mainly because the salvaging of scrap fabric was, at best, an uncertainty, although the French accumulated a considerable quantity.

Summary

Many processes utilized in the war for the manufacture and use of cellulose acetate and nitrocellulose dopes for the coating of aircraft fabrics have been made public since the signing of the armistice. Through the issuance of official governmental publications and articles in the technical journals, our European allies have taken a leading part in this commendable procedure.

In this brief review an account is given of the commercial development, in Europe, of cellulose acetate, certain of the physical and chemical characteristics required for its use in dopes, cellulose acetate solvents, diluents, thermoplastic combinations, pigmentation, camouflage, application of dopes, and recovery of solvents and cellulose acetate from discarded fabric.

Bibliography

1—The Chief of the Air Service has granted permission for the release of three expurgated sets of *Report* 13 2-8, which work is being completed under the direction of Mr. E. C. Worden.

2—J. Ramsbottom, Report of Advisory Committee for Aeronautics (British), 1914.

3—*Rev. Chim. Ind.*, 1920, No. 7, 177.

—Fifth Report from the Select Committee on National Expenditure (British Parliament), 1918. See also *J. Soc. Chem. Ind.*, 38 (1919), 317*r*.

5—*Chem. Age (London)*, 1 (1919), 275.

6—*Color Trade J.*, 5 (1919), 50; *Chem. Age (London)*, 1 (1919), 279.

7—See E. Worden, *J. Soc. Chem. Ind.*, 38 (1919), 370*t*, note 31, and Brit. Patent 20,978, 20,979 (1911); 21,376, 22,645 (1912); 118,891 (1918); 126,347, 127,678, 128,215, 128,274, 131,669, 132,283, 133,353 (1919); 154,334 (1920); U. S. Patent 1,315,480, 1,325,931 (1919); 1,353,384, 1,353,385, 1,363,763 (1920); French Patent 413,671, 413,787, 430,606, 432,046/15,894, 432,047/15,719, 432,264/16,854, 432,264/19,678, 448,342, 448,342/17,674, 494,453, 498,726; Swiss Patent 65,051 (1911); Can. Patent 155,724 (1914); 191,800, 191,801, 191,802 (1919); Holl. Patent Appl. 683 (1912); Hung. Patent Anm. D-2145 (1912); Austrian Patent Appl. 120 (March 9, 1911); Portuguese Patent 8,348 (1912).
See also E. Worden, "*Technology of Cellulose Esters*" (1921), I, 3000, 3001, 3008, 3012, 3013, 3014, 3020, 3023, 3026, 3028, 3030, 3039, 3040, 3041, 3043, 3045, 3047, 3048, 3051, 3060, 3061. See also M. Deschiens, *Chimie & industrie*, 3 (1920), 591.

8—U. S. Patent 1,030,311 (1912); 1,191,439 (1914); 1,258,913, 1,216,462 (1915); U. S. Appl. Ser. 31,707 (1915); Brit. Patent 25,893 (1912); 13,696 (1914); 7,763, 7,773, 8,046, 10,822 (1915); 128,911 (1919); French Patent 437,240 (1911); 473,399, 477,620, 478,436 (1914); Addn. 20,072 (1915) to 473,399 (1914); Swiss Patent 59,412 (1911); 68,996, 71,695 (1914); 71,991, 77,663, 78,108 (1915); D. R. P. 258,879 (1910); D. R. P. Anm. (June 25, 1913); (June 12, 1914); (June 12, 1915); Can Patent 139,046 (1912).

9—E. Worden, *J. Soc. Chem. Ind.*, 38 (1919), 370*t*.

10—*Z. angew. Chem.*, 32, (1919), 66, 76, 82; abst. *C. A.*, 13 (1919), 2670; *J. Soc. Chem. Ind.*, 38 (1919), 355*a*.

11—*J. Soc. Dyers Colour.*, 36 (1920), 19.

12—*J. Ind. Eng. Chem.*, 12 (1920), 861; *Chem. Met. Eng.*, 23 (1920), 861.

13—British Air Board Specification D-6, June 1918.

14—*The Lancet*, December 26, 1914.

15—*Trans. Med. Soc. Lond.*, 38 (1915), 129. See also W. Wilcox, *Brit. Med. J., February* 26, 1916; T. Legge, *J. Ind. Hyg.*, 2 (1920), 121; abst. *C. A.*, 15 (1921), 282.

16—Brit. Patent 124,763, 124,844, 126,989 (1916); 131,369 (1918); *J. Soc. Chem. Ind.*, 38 (1919), 319*a*, 531*a*, 759*a*; *C. A.*, 13 (1919), 1771.

17—U. S. Patent 1,173,931; Fr. Patent 461,058, 479,387; abst. *Bull. soc. encour. ind. nat.*, 121 (1914), 1871; *J. Soc. Chem. Ind.*, 33, (1914), 320; 34 (1915), 75; 35 (1916), 465, 1164; *C. A.*, 9 (1915), 1253; 10, (1916), 1104, 2308. See also *Chimie & industrie*, 1 (1918), 560; 3 (1920), 440. A. Fuchs, *Chimie & industrie*, 3 (1920), 167.

18—*J. Ind. Eng. Chem.*, 10 (1918), 135.

19—British Air Board Specification D-100, March 1918.

20—On use of acetanilide as softener, see British Emaillite Company and J. Goldsmith, U. S. Patent 1,298,199; Brit. Patent 124,515 (1916); abst. *J. Soc. Chem. Ind.*, 38 (1919), 378*a*, 472*a*; *C. A.*, 13 (1919), 1771.

21—J. Grolea and J. Weyler, Brit. Patent 123,712 (1918); abst., *J. Soc. Chem. Ind.*, 38 (1919), 714*a*.

22—See also A. Zimmer, J. Bryce and G. Davies, Brit. Patent 124,807 (1916; abst., *J. Soc. Chem. Ind.*, 38 (1919), 379*a*; *C. A.*, 13 1771.

23—Cellon, Ltd., Tyrer & Co., Ltd., T. Tyrer, Brit. Patent 130,402 (918); abst., *J. Soc. Chem. Ind.*, 38 (1919), 714*a*.

24—See H. Fenton and A. Berry, *Proc. Cambridge Phil. Soc.*, 20 (1920), 16.

25—S. Groves and T. Ward, Brit. Patent 128,659 (1917); abst., *J. Soc. Chem. Ind.*, 38 (1919), 647a; *C. A.*, 13 (1919), 3028. Suggested zinc chloride and calcium chloride as fire retardants in nitrocellulose dopes.

26—Formerly Chef de Service Chimique, Section Technique de l'Aeronautique.

27—See G. Ward, Brit. Patent 128,658 (1917); abst., *J. Soc. Chem. Ind.*, 38 (1919), 647*a*.
Chem. Ind., 38 (1919), 647*a*.

28—Third Annual Report of the National Advisory Committee for Aeronautics, 1918. For Walen's article on tapes see Fourth Report, 1919.

29—*British Engr. Standard Assoc. Bulletin* 83 (April, 1918).

30—See L. Vignon, *Compt. rend.*, 170 (1920), 1322.

31—For a pigmented dope formula see A. Barr and H. Lazell, Brit. Patent 136,641 (1918); abst., *J. Soc. Chem. Ind.*, 38 (1919), 834*a*.

32—For physico-chemical discussion of recovery methods see M. Ponchon, *Chimie & industrie* 1 (1918), 481; abst., *C. A.*, 13 (1919), 364. For other solvent recovery processes see E. Worden, "Technology of Cellulose Esters," 1921, I, 2553-2558. See also M. Deschiens, *Rev. prod. chim.*, 23 (1920), 237.

33—U. S. Patent 1,315,700, 1,315,701; Brit. Patent 128,640, 131,938 (1917); Can. Patent 195,703 (1920); abst., *C. A.*, 13 (1919), 2983; 14 (1920), 326; *J. Soc. Chem. Ind.*, 37 (1918), 194*a*; 38 (1919), 612*a*, 751*a*, 855*a*. A. Daniel and J. Bregeat, Brit. Patent 127,309 (1917); abst., *J. Soc. Chem. Ind.*, 38 (1919), 521*a*; *C. A.*, 13 (1919), 2428; French Patent Appl. 83,674 and Addn. 9,304 (1916), 91,720 and Addn. 10,479 (1917); Belg. Patent 16,956 (1917); 18,388 (1917). See also booklet of Bregeat Corporation of America; P. Razous, *Industrie chimique* 6 (1919), 14, 48; abst., *C. A.*, 13 (1919), 27[illegible]; *Caoutchouc & Gutta-percha*, 16 (1919), 9758; abst., C. A., 13 (1919), 1548.

34—J. Schmidlin and R. Lang, *Ber.*, **43** (1910), 2806; abst., *C. A.*, **5** (1911), 487; *Ber.*, **45** (1912), 899; abst., *C. A.*, **6** (1912), 2428.
T. Zincke and W. Gaebel, *Ann.*, **388** (1911-1912), 299; abst., *C. A.*, **6** (1912), 1753.

35—I. Masson and T. McEwan, *J. Soc. Chem. Ind.*, **40** (1921), 32*t*.

36—E. Barbet et Fils et Cie., Brit. Patent 101,723, 101,875 (1916); 117,259 (1918); U. S. Patent 1,326,432; abst., *J. Soc. Chem. Ind.*, **37** (1918), 45*a*; **38** (1919), 521*a*; **39** (1920), 145*a*; *C. A.*, **11** (1917), 280; **12** (1918), 2417.

37—French Patent Appl. 103,588 (August 26, 1918).

38—Brit. Patent 2,365 (1918); abst., *J. Soc. Chem. Ind.*, **37** (1918), 111*a*.

Motor Fuel from Vegetation[1]

By T. A. Boyd
GENERAL MOTORS RESEARCH CORPORATION, DAYTON, OHIO

For operating the motors of the country an enormous and ever increasing amount of liquid fuel is required. This amount of fuel is so large that not only has great activity in the production of crude oil been necessary to meet the demand but the reserves of crude oil are also being rapidly depleted. The yearly production of petroleum has become so large that exhaustion of its reserves in the United States threatens to occur within a few years. The object of this paper is to present the danger with which motor transportation is threatened, with the hope of directing further attention to a possible means of solving this problem, which is of such vital importance to the country.

THE PRESENT MOTOR FUEL SITUATION

The number of automobiles and trucks in use in the United States has increased from about 1,000,000 in 1912 to about 9,000,000 in 1920, an average increase of over 1,000,000 a year. Crude oil, the principal source of fuel for motor vehicles, has shown an increase in domestic production during the same period from about 220,000,000 barrels to 440,000,000 barrels a year; so that, while the number of motor vehicles in use has increased about ninefold, domestic crude oil production has only doubled. The relation between motor vehicles in use, as shown by registration figures, and the production of crude oil is given graphically in Fig. 1.

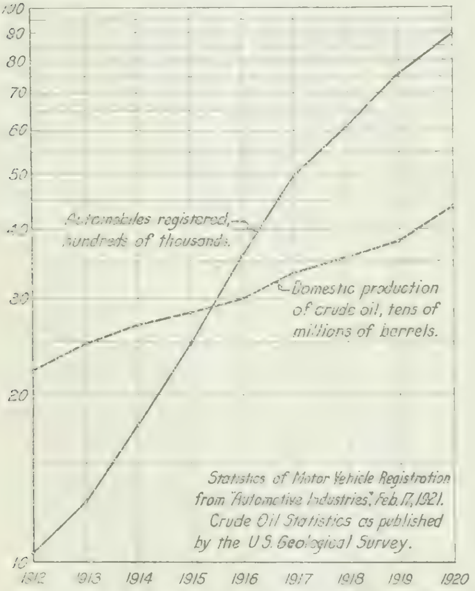


Fig. 1—Relation between automobiles registered and production of crude oil

In Fig. 2 the relative growths of the three factors, motor vehicle registration, crude oil production, and gasoline production, are compared with 1909 values. The production of crude oil has increased since 1909 about 140 per cent, and that of gasoline about 800 per cent, but the number of automobiles registered has increased 2570 per cent.

The normal gasoline content of the crude oil produced in the United States is around 20 per cent.[1] The actual production of gasoline has exceeded this percentage of the crude since 1917. Refiners have met the rapidly in-

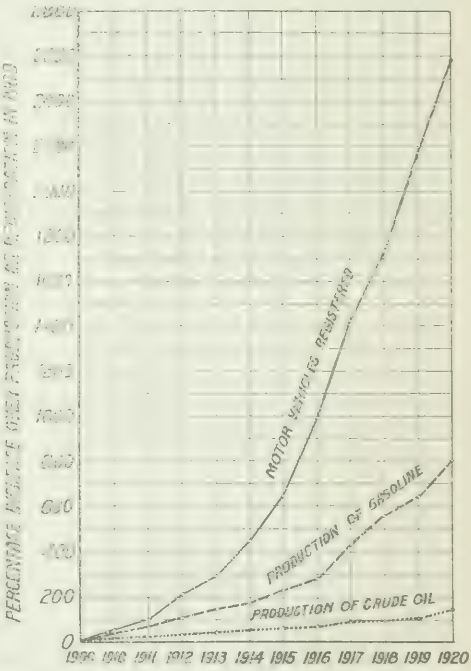


FIG. 2—PERCENTAGE INCREASES IN MOTOR VEHICLES REGISTERED, PRODUCTION OF CRUDE OIL, AND PRODUCTION OF GASOLINE, COMPARED WITH 1909[1]

[1] U. S. Bureau of Mines, *Bulletin* 191, 13; *Automobile Industries* (Feb. 17, 1921), 346; recent statistics, U. S. Bureau of Mines and Geological Survey.

---

[1] Read before the Cellulose Section at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[1] David White, *J. Soc. Automotive Eng.* 43, (1919), 61.

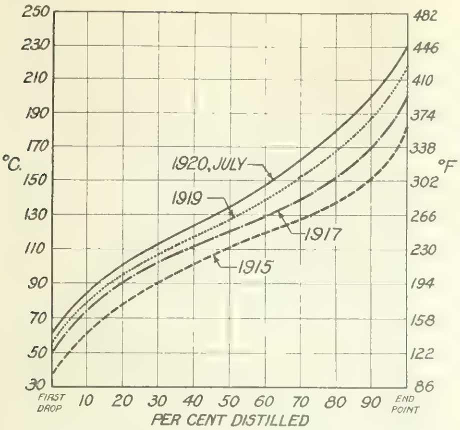


Fig. 3—Change in Volatility of Motor Gasoline, 1915 to 1921[1]

[1] U. S. Bureau of Mines data taken from "The Trend of the Oil Industry in 1920," by Joseph E. Pogue, AUTOMOTIVE INDUSTRIES, (February 17, 1921) 404.

creasing demands for gasoline from a production of crude oil which did not keep pace with the demand for motor fuel:

1—By increasing the average boiling point of gasoline
2—By extracting liquid hydrocarbons from natural gas
3—By cracking heavy petroleum oils

There is a limit above which the average boiling point of gasoline cannot be raised; although, at present, no one is able to predict accurately just what this limit is. The amount of casinghead gasoline which can be manufactured is small at best, but it is very valuable both because of the low initial it gives to commercial gasoline on being blended with it, and because by proper blending it makes available for motor fuel a certain amount of high boiling oil which could not otherwise be used for this purpose. The cracking of heavy petroleum oils as it is now conducted is wasteful from a fuel conservation standpoint, and the successful operation of a cracking plant depends upon the margin between the price of fuel oil and that of gasoline. The rapid increase in the use of fuel oil for certain land and marine purposes is gradually making it an essential for a class of transportation that will use a large amount of it and that represents a high type of demand which can command a supply on a price basis.

Of the means which have been used to increase the yield of gasoline above the normal 20 per cent from the crude oil, and which have been enumerated above, the most effective one is the simple expedient of cutting deeper into the crude. The general trend of the average boiling point of gasoline has been upward ever since the early days of automobiles, when the fuel used was 76° gasoline. No authentic distillation data are available for the motor fuel in use prior to 1915. In Fig. 3 are shown average distillation curves of commercial motor gasoline in the United States since 1915. The increase in distillation temperatures from 1915 to 1920, as shown in Fig. 3, represents a change in composition of gasoline which corresponds to a marked increase in the production of straight run gasoline from a given amount of crude oil.

This increase in the end-point or the average boiling point of motor gasoline has introduced some serious problems which the automotive industry has been called upon to face. As gasoline has become heavier, distribution and vaporization have become increasingly difficult; it has become harder to start motors; carbonization of cylinders has greatly increased; and contamination or dilution of the oil in the crankcase has become much worse. But of most importance is the increased tendency of the fuel to knock as its distillation temperature rises. Distribution and vaporization are being accomplished to a great extent by the application of heat in various ways; but still further improvements along this line are essential, and they are being made as the results of experimental work point the way. A number of expedients for starting cold motors when using commercial gasoline are now in use, and further improvements are constantly being made. Dilution of the lubricating oil, which is aggravated by high boiling fuel, is a problem which in the light of experience appears capable of being satisfactorily solved. These difficulties are present on account of physical reasons, and they can be corrected by mechanical or physical means.

The fuel knock, however, under given conditions of pressure and temperature is a function of the chemical composition of the fuel. The paraffin hydrocarbons which make up the greater percentage of commercial gasolines are comparatively bad from a knocking standpoint, and their tendency to knock increases with boiling point. Since the fuel knock increases both with compression and temperature, this characteristic of commercial motor fuel limits the initial compression at which it may be used. In limiting the compression it limits the efficiency at whch the motor operates, in accordance with the curve in Fig. 4.

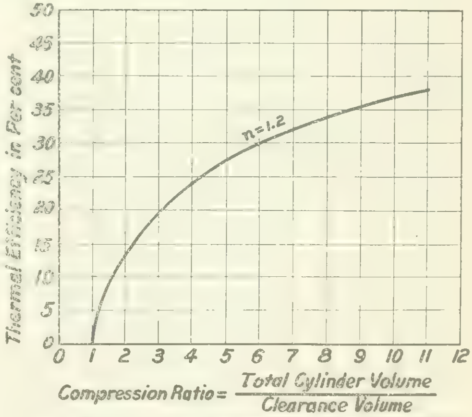


Fig. 4—Relations between Thermal Efficiency and Compression Ratio in an Internal Combustion Engine.[1]

[1] Dickinson, *J. Soc. Automotive Eng.*, 12 (1919), 228.

The standard compression ratio for automobile engines is now about 4:1. At the maximum compression reached with this compression ratio the knock is an inconvenience, but the seriousness of the knock lies in the fact that it interposes a barrier to any increase in compression above the present standard, and thereby limits the thermal efficiency at which motors can be made to operate. The rising average boiling point of motor gasoline introduces additional difficulties on account of the fuel knock in proportion to the increase in boiling point. This apparent barrier to more efficient utilization of gasoline as a fuel for internal combustion motors is capable of solution, at

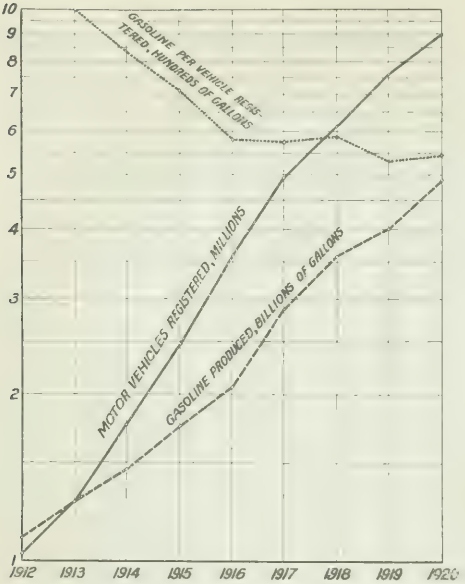


Fig. 5—Relation between motor vehicles in use and gasoline production[1]

[1] U. S. Bureau of Mines, BULLETIN 191; AUTOMOTIVE INDUSTRIES, (February 17, 1921), 306; recent statistics, Bureau of Mines.

least to some extent, and considerable progress has already been made along this line.[1]

In Fig. 5 is shown the relation between motor vehicles in use and gasoline produced in the United States. The registration figures do not include a number of large users of gasoline, such as airplanes; tractors, of which more than 425,000 are estimated to have been in operation during 1920;[2] motors boats, of which 200,000 are estimated to have been in service in 1920;[3] etc. There is seen to be a considerable divergence between the curve of motor vehicles registered and that of gasoline produced. This divergence has occurred in spite of the fact that, as shown above, the average boiling point of gasoline has been gradually rising. Furthermore, the percentage of gasoline produced from the crude oil run by refineries in the United States has gradually risen from about eleven in 1909 to eighteen in 1914 and twenty-seven in 1920. In interpreting the curve for 1920, it should be noted that high prices stimulated a phenomenal production of crude oil last year and that the sale of automobiles suffered from a serious depression during the last four months of the year.

As an illustration of the effect of demand on the endpoint or the average boiling point of gasoline, the following figures are of interest. These figures have been taken from the second and third semi-annual gasoline surveys made by the United States Bureau of Mines, and they give average boiling points in ° F.[4]

	January 1920	July 1920	January 1921
Chicago	270	275	264
San Francisco	262	270	265
New York	261	272	265
Washington	267	279	270
Salt Lake City	270	286	285
Pittsburgh	257	275	244
New Orleans	254	285	272
Average	264	278	266

While, of course, a part of the rise from 264 in January to 278 in July was due to the usual seasonal change in the quality of gasoline, a part was also due to the taking of more gasoline from the crude in order to meet a demand for motor fuel, which was very large during the spring and summer of last year. The ratio of gasoline produced in January 1920 to the crude run by refineries during the same month was about 0.26. This ratio reached a maximum in June, at 0.283.[1]

Stocks of gasoline usually reach a minimum point in September or October. In spite of the phenomenal production of crude oil during 1920, and the rise in average boiling point of motor gasoline during the first half of the year, stocks of gasoline at the end of September were lower than at the same time in 1919, and very little higher than at the end of September 1918, which was during the war and about the time of the gasolineless Sundays. The depressed condition throughout the country during the latter part of 1920 reacted on the oil industry and influenced the quality of gasoline. The general reductions in the price of gasoline which have occurred throughout the country during the past four months are an indication of the conditions which have influenced its quality to the extent of bringing its average boiling point back almost to the January 1920 figure. But it is to be expected that a return to normal conditions will bring with it further increases in the average boiling point of motor gasoline, especially since very little prospecting or drilling of new wells has been done so far this year.

The general trends which have been given above indicate that the raising of the average boiling point of gasoline has been a necessity rather than a matter of choice with refiners. It was necessary that fuel be supplied to the motor vehicles in use, the number of which has been growing at a much faster rate than has the production of crude oil (Figs. 1 and 2). It is impossible to predict accurately what the future will be, but the automobile, the truck, and the tractor have become necessities, and it is certain that they will be exploited still further.

In order to keep up production, the oil industry must continually find new sources of crude oil. It is estimated that one-fourth of the oil produced comes from wells less than a year old.[2] Some large producers of crude oil have expressed the belief that they will be able to find plenty of new sources of oil.[3] The United States Geological Survey has made a careful estimate of the unmined supply of crude oil in the United States,[4] and their estimate, which is based on an exhaustive survey, together with the amount of crude oil that had been taken from the ground up to January 1, 1921, is given in Fig. 6. The unmined supply at that time, which was roughly 6,000,000,000 barrels, will be exhausted in about 13 years if the rate of production is maintained at the 1920 figure (about 443,000,000 barrels).

---

[1] Thomas Midgley, Jr., "The Combustion of Fuel in the Internal Combustion Engine," *J. Soc. Automotive Eng.*, 7 (1920), 489.

[2] An analysis of the farm market for motor trucks, published by the Goodyear Tire & Rubber Co.

[3] American Petroleum Institute, *Bulletin* **145**, February 26, 1921.

[4] *Oil Paint and Drug Reporter*, Petroleum Section, August 16, 1920, and February 14, 1921.

[1] U. S. Bureau of Mines, Refinery Statistics for 1920.

[2] R. D. Persen, "Production, the Present," American Petroleum Institute, *Bulletin* **132** (December 10, 1920), 31.

[3] Thos. A. O'Donnel, President of the American Petroleum Institute, "Production, the Future," American Petroleum Institute, *Bulletin* **132** (December 10, 1920), 32; Henry L. Doherty, "The Future of the Oil Business," *ibid.*, 45.

[4] David White, "The Unmined Supply of Petroleum in the United States," *J. Soc. Automotive Eng.*, **12** (1919), 361.

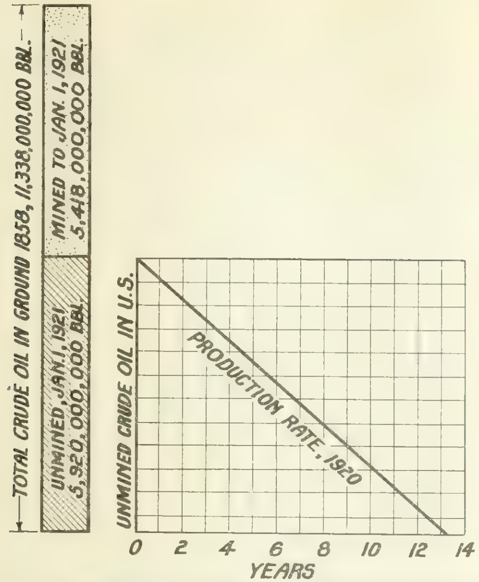


Fig. 6—Unmined Supply of Petroleum in the United States as Estimated by the U. S. Geological Survey[1]

[1] Data from David White, *J. Soc. Automotive Eng.*, 12 (1919), 361, and U. S. Geological Survey production statistics.

Assuming that the estimate of the Geological Survey is correct, it can be but a very few years until the total amount of crude oil that has been mined will approach the amount of this estimate. But, before the total amount of crude oil mined can reach the amount of crude oil originally in the earth, the slope of the production curve must fall off, on account of the reduction in the number of new producing wells being brought in and the gradual decline of old wells. This will bring the country face to face with a real shortage of motor fuel, and at the best it will make us dependent upon foreign supplies of oil. Even if the estimate of the Geological Survey should be 75 per cent in error, which Dr. David White of the United States Geological Survey thinks is extremely improbable,[1] the unmined supply of petroleum in the United States would last only twenty-three years at the rate at which it was mined in 1920.

Dr. George Otis Smith, director of the United States Geological Survey,[2] has estimated that if the burden of supplying the 50,000,000 horsepower, which he gives as the average requirement of the United States, should fall upon the coal mines, on the basis of the best steam practice of today, the present power requirements of this country could be met for 57,000 years. If this burden were to fall upon our supply of oil, however, on the same basis of the best present-day steam practice, he estimates that the oil reserves of the United States would last only nine years and three months.[3]

Motor Fuels Other Than Petroleum Oils

In view of the petroleum oil situation outlined above, conservation of materials suitable for motor fuel would appear to be a matter of vital importance. As a means toward such conservation any liquids other than petroleum oils that are suitable for motor fuels should be utilized to the fullest possible extent, and an increase in the production of such materials should be encouraged. Two liquids which are now used as motor fuel to some extent, *viz.*, benzene and alcohol, appear to be very promising allies to petroleum oils as fuels for internal-combustion engines.

SHALE—It is probably only a matter of time until some motor fuel will be manufactured in this country from shale. But oil does not occur in shale as such, and it must be produced from the shale by a cracking process. Furthermore, the oil so obtained usually contains but a small percentage of low boiling material that is suitable for motor fuel, and the production of an increased percentage of light oil necessitates further cracking. The resulting material is high in content of olefines and must be blended with a large percentage of a saturated oil before it can give satisfaction as a fuel for automotive engines. It would seem that the greatest value of shale is as a source of fuel oil rather than of motor fuel. Conditions in England and other countries where motor fuel is produced from shale are quite different from those in the United States. The price of motor fuel in England during the latter part of 1920 was more than four shillings per imperial gallon. In spite of this price, and of the facts that a large percentage of their motor trucks are steam driven and that they have had a domestic production of gasoline from shale for many years, the motor fuel situation in England last year, as in other European countries, was critical.

BENZENE—Benzene, or motor benzene, which is a refined light oil, makes a desirable motor fuel when blended with gasoline. Such blends give a mileage about equal to gasoline, and they give operation that is very smooth and free from fuel knock. However, the present production of light oil in the United States is less than 3 per cent of the amount of gasoline that is produced. If all the bituminous coal mined in the United States in 1918 (579,386,000 tons) had been treated for the production of motor fuel, the yield would have been less than one-fifth of the gasoline produced in the United States in 1920.[1]

ALCOHOL—The most direct route which we now know for converting energy from its source, the sun, into a material that is suitable for use as fuel in an internal-combustion motor is through vegetation to alcohol. While it now appears that alcohol is the only liquid from a direct vegetable source that combines relative cheapness with suitability, any liquid material which can be prepared from vegetation and which is right from the standpoints of cost, boiling point, heating value, and operation in an internal-combustion motor will serve the purpose. The use of gasoline or benzene is drawing on the reserves which nature has stored up, but which have required long periods of time for formation. Because a long period of time is necessary for the formation of these materials the supply cannot be renewed. Alcohol is obtained from a source the supply of which can be renewed from year to year and which does not depend upon a definite amount of raw material that has been stored up in the past.

Alcohol as a Motor Fuel

Alcohol has been used as a motor fuel to a considerable extent and it has been found to be suitable for this purpose, and indeed it has certain advantages. Its combustion is marked by cleanliness and freedom from any deposition of carbon in the combustion chamber. Because it boils at a definite and comparatively low temperature it can be well distributed in multi-cylinder motors. On account of its low boiling point it should give no trouble from dilution of crankcase oil. Alcohol will stand very high initial compressions without knocking, and at high compressions its combustion is smooth and highly satisfactory. Because of the high compression at which alcohol may be used the available horsepower of a definite size of motor is much greater with alcohol than with motor gasoline, if each be run at its most economical compression.

---

[1] "Petroleum Resources of the World," *Sibley Journal Eng.*, November 1920, 156.

[2] "A World View of the Oil Supply," American Petroleum Institute, *Bulletin* 132 (December 10, 1920), 8.

[3] The United States Bureau of Mines has estimated that only about 20 per cent of the oil is recovered from the earth by present methods of extraction (G. A. Burrell, *Oil Gas J.*, October 22, 1920, page 84). It is unlikely that all of this oil can be recovered by any means, but it seems likely that a process will be devised for making a higher percentage of this oil available.

[1] The average yield of light oil from a ton of coal [illegible] "Mineral Resources of the United States," 1916, II, 515.

The curve in Fig. 4 shows how an increase in initial compression affects thermal efficiency. Since alcohol does not knock even at compression ratios in excess of 8.2:1, which at wide open throttle and average motor speeds gives a compression considerably above 200 pounds per square inch, it may be run at such a compression that it will give as good fuel economy as gasoline, although its heating value is considerably lower than that of gasoline. Comparative tests of alcohol and gasoline run at 180 and 70 pounds initial compression, respectively, have shown that, in general, equal volumes of these fuels are required per brake horsepower-hour.[1]

DISADVANTAGES OF ALCOHOL—As a motor fuel alcohol has certain disadvantages which should be enumerated here:

1—*Low heating value—around 80,000 B.t.u. per gallon, as compared to about 120,000 B.t.u. per gallon of gasoline.* Because of the freedom of alcohol from tendency to knock, this difficulty may be overcome by initial compressions which are high enough so to increase the thermal efficiency that the output per gallon of alcohol is equal to that of a gallon of gasoline. Such a motor, however, would be a special device which could not run on gasoline, and which, therefore, would not be feasible under present conditions.

2—*High latent heat and low vapor pressure make it hard to start.* This difficulty has been overcome by blending with light petroleum oils, for which purpose casinghead gasoline is very suitable.

3—*Is absorbed by cork carburetor floats, thus rendering them useless.* [illegible] *deposited in fuel system, and thereby clogs screens in the fuel lines.* If alcohol alone or blended is used as a fuel it necessitates metal carburetor floats and clean fuel lines.

4—*Will not blend with petroleum oils unless it is either practically free from water, or unless a binder is used.* A number of materials have been used to blend 95 per cent alcohol with petroleum oils, of which benzene is probably the best. The unsaturated materials in cracked petroleum oils are effective and cheap, but the final percentage of unsaturation must be kept low so as not to cause motor trouble resulting from the polymerization of such materials to gums or tars.

While some of the above difficulties are real, from the standpoint of a large percentage of the nine million motors now in use, they are such that old and new motors can readily be adapted to utilize alcohol as a fuel at a much faster rate than the production and distribution of alcohol can be increased. So far alcohol as a motor fuel has been of very minor importance. The production of denatured alcohol in the United States has never exceeded 100,000,000 gals. a year. While this is apparently a large figure, it is only about 2 per cent of the volume of motor fuel consumed in the United States last year.

SOURCES OF INDUSTRIAL ALCOHOL

At present the principal source of industrial alcohol is the blackstrap molasses obtained in the refining of cane sugar. The yearly consumption of Cuban and Porto Rican blackstrap in the principal American plants is about 130,000,000 gals. a year.[1] Other sources of alcohol are starchy food stuffs and waste cellulose-containing material, such as wood. Two plants manufacturing alcohol from waste wood have been in successful operation in this country for the last few years.[2] These plants obtain a yield of from 15 to 25 gals. of 95 per cent alcohol per ton of dry wood at a cost of about 25 cents per gallon. From the wood which is absolute waste, that is, which is not utilized for reworking or for fuel, it is estimated that there could be produced 240,000,000 gals. of 95 per cent alcohol. This is on the basis of 15 gals. per ton of dry wood, utilizing only soft wood waste.[3]

The large amount of motor fuel required seems to exclude the possibility of preparing any considerable percentage of the necessary amount from foodstuffs. In illustration of this statement the following figures are of interest.[4]

Average annual U. S. production of corn, 1913-1919, bushels	2,740,000,000
Average annual acreage in corn, 1913-1919	106,000,000
Alcohol from the corn at 2.75 gallons per bushel	7,500,000,000

The heating value of this amount of alcohol is about equal to that of 5,000,000,000 gals. of gasoline. The production of gasoline in the U. S. during 1920 was very close to this amount, it having been about 4,900,000,000 gals. The average acreage in corn as given above is equal to 166,000 sq. miles, which is more than four times the total area of Ohio. In view of the fact that the possible alcohol production from corn represents close to 60 per cent of the total possible amount of alcohol that could be prepared from all of the starch and sugar containing foodstuffs produced in the United States, and that such a large acreage is required for its production, the possibility of a sufficiently large increase in production of such materials to be diverted to the manufacture of motor fuel seems very unlikely. At any rate if large quantities of motor fuel are to be prepared from vegetation another material, if not instead of foodstuffs, at least in addition to foodstuffs, must be relied upon as a source.

CELLULOSE AS A SOURCE OF MOTOR FUEL

This material is cellulose. It is suitable from a chemical standpoint, it is readily available, it is easily produced, and its supply is renewable. By the return to the soil of the refuse material from the production of alcohol the soil would lose none of its constituents that are necessary in order to keep up its fertility. But a number of large problems will have to be solved before cellulose can be relied upon as a source of motor fuel.

The largest of these problems is the development of a commercial process that will give a good yield of alcohol from cellulose. This is a problem which must be solved by men trained in chemistry. A yield of 20 gals. from a ton of material which is about 50 per cent cellulose is considerably less than one-half of what it should be. A yield of 50 gals. of alcohol from a ton of wood or other cellulose containing material would give the manufacture of motor fuel from such material an entirely different aspect. If a yield of 60 to 65 gals. of motor fuel could be obtained from a ton of cellulose-containing material by a process that would compare favorably in cost with that now used to make alcohol from wood its success would be assured, and the danger of a serious shortage of motor fuel would disappear.

---

[1] United States Bureau of Mines, *Bulletin* 43, [illegible]

[1] Geo. M. Appell, "Alcohol Production from Molasses," *Chem. Age (N.Y.)*, 29 (1921), 53.

[2] E. C. Sherrard, "Manufacture of Ethyl Alcohol from Wood Waste," *Chem. Age*, 29 (1921), [illegible]

[3] E. C. Sherrard, private communication "Brief Report on Wood Waste Available for Production of Ethyl Alcohol," Forest Products Laboratory.

[4] Based on statistics of U. S. Dept. of Agriculture.

Of almost equal importance with the development of a process is the problem of supply of raw material. On the basis of 50 gals. to the ton, 100,000,000 tons of raw material would be required to yield the almost 5,000,000,000 gals. of motor fuel produced in the United States last year. This is more than one-fifth of the amount of bituminous coal mined in the United States in 1919. Yet it is slightly less than the weight of hay produced in this country in the same year. Not only must there be a plentiful supply of raw material, but it must also be cheap. If it should cost one cent a pound or twenty dollars a ton the cost of the raw material alone would be 40 cents a gallon, even on the basis of 50 gals. to the ton. The supply of raw material must be constant enough to permit plants to be operated throughout the year, and the distance over which it is transported must be such that transportation charges will be low. The solution of the problem of supply will depend largely on the success that is met with in developing a satisfactory process, and it may lie in the utilization of waste materials and the production of rapid growing plants in a climate that permits growth during the whole or a large part of the year.

It is important that a change in government regulations be secured, in order both to simplify and cheapen this work. The adaptation of motors to utilize alcohol efficiently as fuel will come with the development of its distribution and use as a fuel. There are no doubt a number of other and smaller problems which may require considerable effort, but which will be solved if the major difficulties are overcome.

The large amount of research work which has been done in the past by a number of different investigators in an effort to make alcohol from cellulose has resulted in certain definite and important discoveries. It has been demonstrated that cellulose can be changed almost quantitatively to dextrose, which in turn can be converted to alcohol.[1] While it has been found that different materials serve as reagents for making this hydrolysis, only strong acids have so far been found to effect an approximately quantitative conversion of cellulose to dextrose. The cost of these materials and the difficulty of their recovery makes a process for the manufacture of motor fuel which is based upon their use far from commercial. But cellulose-containing materials give a considerable yield of fermentable sugar upon being subjected to the action of very dilute acids at elevated temperatures and under pressure. This is the basis of the process that is now used in making alcohol from waste wood, and which gives a yield of from 15 to 25 gals. of alcohol per ton of dry wood.[2] The fact that a quantitative conversion of cellulose to dextrose can be accomplished shows the possibility of this material as a source of alcohol, if a process can be found which will approach on the one hand, the cheapness of the dilute acid process and, on the other, the almost quantitative yields of the strong acid process.

The progress which has so far been made in the manufacture of alcohol from cellulose, and the great necessity for and possibilities of such a process, justify a large amount of further research being put into an effort to make the preparation of a liquid motor fuel from cellulose a commercial success. And from all indications it will require a great amount of further research work to accomplish this result. The success of the efforts which are being made to establish or determine the chemical structure of the cellulose molecule should make a large contribution to the advancement of cellulose chemistry. If the production of a liquid motor fuel from cellulose can be accomplished on a large scale, it will add greatly to the importance and burden of this widely distributed and already very valuable product of nature, as well as solve the problem of the future supply of motor fuel.

The Role of the Chemist in Relation to the Future Supply of Liquid Fuel[1]

By Harold Hibbert

Department of Chemistry, Yale University, New Haven, Connecticut

According to a recent report of the United States Geological Survey, if the rate of production of crude oil in 1920, namely, about 443,000,000 barrels, continues to be maintained our supply of crude oil will have become entirely exhausted in about 13 years. Does the average citizen understand what this means? In from 10 to 20 years this country will be dependent entirely upon outside sources for a supply of liquid fuel for farm tractors, motor transportation, automobiles, the generation of heat and light for the thousands of country farms, the manufacture of gas, lubricants, paraffin and the hundreds of other uses in which this indispensable raw material finds an application in our daily life.

It must be frankly admitted that at the present moment there is no solution in sight, and it looks as if in the rather near future this country will be under the necessity of paying out vast sums yearly in order to obtain supplies of crude oil from Mexico, Russia and Persia. It is believed, however, that the chemist is capable of solving this difficult problem on the understanding that he be given opportunities and facilities for the necessarily laborious and painstaking research work involved.

We already know, for example, that it is possible to obtain alcohol from corn and a variety of grains on the one hand, and from wood, on the other. Such a synthesis of liquid fuel is, in the last resort, nothing more than the utilization of the energy supplied by the rays of the sun. Through this agent the young plant is developed, crops are grown and harvested and from both a liquid fuel, namely alcohol, can be manufactured.

There appears to be no doubt that if the latter could be obtained at a reasonable cost and in quantities sufficient for the purpose the problem would be solved, since the evidence is fairly conclusive that alcohol is capable of replacing gasoline with but little alteration necessary in the present type of engine design.

The problem thus becomes one of finding a sufficient supply of suitable raw material. As indicated by Boyd,[3] the available quantity of blackstrap molasses is sufficient to supply only a very small fraction of the alcohol required, while the utilization of cereals cannot be undertaken without seriously endangering the nation's food supply. On the other hand, as indicated in the interesting communications of both Boyd and Whitford,[4] it would seem that cellulose in one form or another should be capable of filling the role.

It is known that when wood (which consists of about 50 per cent cellulose) is treated with acids it is converted into dextrose, which latter, on fermentation, yields ethyl alcohol, one ton of sawdust giving about 20 gallons of alcohol or roughly about 35 per cent of the theoretical quantity. On this basis the supply of wood necessary to produce 4,430,000,000 gallons (the present annual requirement assuming equal value per unit of motive power) would amount to around 221,500,000 tons, equivalent to about 14,760,000,000 cubic feet (assuming a cubic foot of wood to weigh 30 pounds). The total amount of wood available for liquid fuel which could be secured from the forests of the United States without encroachment upon the supply of other forest products is estimated by Profesor Hawley of the Yale Forestry School as amounting to about 11,030,000,000 cubic feet, or roughly 75 per cent of present requirements. This is made up as follows:

---

[1] Read before the Cellulose Section at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[1] Willstätter and Zechmeister, *Ber.*, 46 (1913), 2401; H. Ost, *Ibid.*, 2995.

[2] E. C. Sherrard, *Chem. Age*, 29 (1921), 76.

[3] JOURNAL, 13 (1921), 836.

[4] To be published later.

Waste in the woods and at the mills	4,800,000,000
Losses from fire, insects and fungi (thinnings)	1,730,000,000
Excess of possible growth over annual cut (thinnings)	1,750,000,000
Increased growth due to more intensive crop management (thinnings)	2,750,000,000
TOTAL	11,030,000,000

It is evident from these figures that a considerable percentage of the necessary raw material can be obtained from domestic sources, but is it **available** as the basis of a commercial proposition? No definite figures are obtainable as to the cost of transporting this enormous quantity of waste lumber to suitable locations for conversion into alcohol, but the evidence indicates that it would be prohibitive under present conditions.

As stated above, the present yield of alcohol is only about 20 gallons per ton of wood, whereas, theoretically, it should be around 60. Furthermore, the present cost of conversion, not assuming any value for the wood, cannot amount to less than approximately 20 cents per gallon. If the chemist could improve the yield considerably there is the possibility of decreasing this to around 10 cents, whereby the utilization of a wide variety of waste cellulosic material would then appear much more inviting.

In view of the cost of "assembling" waste wood it would seem that products such as flax straw, hemp hurds, sorghum, bagasse, corn straw and cobs, sugar cane and sawdust would seem to merit prior consideration, since the cost of "assembling" or "partially assembling" such materials has already been borne in connection with the manufacture of the primary raw product.

The problem as to the best and cheapest source of raw cellulosic material is one which does not admit of easy solution, and the interesting and valuable data in Professor Whitford's paper indicate the great importance of location, namely, tropical growths as compared with those of more temperate zones. His figures relative to bamboo and nipa palms are of interest, since they indicate that an area of the Philippines equal to some 63,300 square miles, if planted to bamboo, could probably be made to yield, by proper selection and cultivation, sufficient cellulose to supply our present demands for liquid fuel in the form of alcohol.

The whole subject requires serious consideration on the part of plant physiologist, cellulose chemist and forester, and the activity at present being shown by the Government in furtherance of reforestation might, with advantage, also be extended to a study of the widest variety of "annuals" as a source of raw material for liquid fuel.

The amount of alcohol obtained on fermentation depends on the yield of sugar from the original cellulosic material, and the higher the content of this the greater the yield. In other words, if the plant physiologist could develop a rapid-growing species of tree or shrub, consisting of an outer cover of cellulose with an inner packing of starch granules, this would presumably go a long way towards providing a solution of the problem of obtaining the necessary raw material.

The task is one of such magnitude that none of the usual chemical manufacturing processes, involving only cheap chemicals and simple apparatus, need be taken into consideration, since the cost of operating by the usual methods would presumably be prohibitive.

A process requiring, for example, only five pounds of any given chemical for the manufacture of 100 gallons of alcohol, would mean for an output of 4,430,000,000 gallons (the present requirements) some 100,000 tons. Similarly, each one per cent of by-products would represent about 20,000 tons. Figures such as these would seem to indicate that the solution of the problem will have to be found in some process, not strictly chemical, and in which there are no by-products which cannot be utilized.

Is there any possibility of finding such? Fortunately there is.

SACCHARIFYING ORGANISMS

Of all chemical processes those carried out by living organisms or enzymes are, comparatively speaking, the cheapest to operate, since the expense for labor, etc., is small, due to the efficient manner in which the tiny organisms operate.

The recent work carried out by Boulard in France on the production of alcohol from starch by the action of certain alcohol-producing fungi indicates a new method of approach from which apparently much may be expected. By the action of these new agents it is claimed that starch may be converted **directly** into alcohol, although in practice it has been found better to use the fungi only for converting the starch into sugar and then to ferment the latter with yeast. Much higher yields are claimed than where the saccharification is effected by acids or by malt. Large-scale experiments are stated to show a yield of 39 to 44 liters of pure alcohol from 100 kilograms of grain compared with 27 to 33 by the acid and 34 by the malt process.

This utilization of fungi for effecting saccharification (conversion of starch, etc. into sugar) would seem to have an important bearing on the subject under discussion.

The evidence which is accumulating with such extraordinary rapidity from day to day relative to the constitution of starch and cellulose[1] indicates that they are relatively simple products, the properties of which it is now possible to **predict** with some degree of certainty. There is also no doubt but that in a short time the nature of the intimate connection between these two materials will have been definitely established. This being the case, the recent work of Pringsheim[2] in Germany on the action of certain fungi on cellulose assumes considerable importance.

This scientist (**not** inventor, technical or consulting chemist, be it noted, guided by the epoch-making work of Buechner on fermentation and the action of ferments, has been able to show that there is a strict analogy between the fermentation of certain carbohydrates such as maltose, cane sugar, starch dextrins, etc., and that of cellulose. In the former cases fermentation takes place in two stages in which two different groups of ferments play an active role. These are the "hydrolytic" and "fermenting" types, respectively. The former bring about the hydrolytic conversion of the maltose, starch dextrins, etc. into glucose, while the latter induce fermentation of this with formation of alcohol.

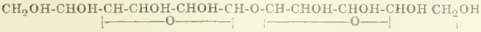
---

[1] Karrer and Naegeli, HELVETICA CHIM. ACTA, 4 (1921), 169, 185, 263; Hess, Z. ELEKTROCHEM., 26 (1920), 232; Karrer and Widmer, HELVETICA CHIM. ACTA, 4 (1921), 174; Freudenberg, BER., 45 (1921); Hibbert, THIS JOURNAL, 13 (1921), 256, 334.

[2] Hans Pringsheim, Z. PHYSIOL. CHEM., 78 (1912), 266.

Similarly under the action of certain ferments, associated with specific microörganisms found in horse-manure, river mud, etc., cellulose is converted into glucose. The first change is brought about by the action of the hydrolytic ferment "cellulase" which converts the cellulose into cellobiose. Under the action of a second ferment "cellobiase" the cellobiose is converted into glucose.

Cellobiose has recently been shown[1] to possess the structure



$$CH_2OH\text{-}CHOH\text{-}CH\text{-}CHOH\text{-}CHOH\text{-}CH\text{-}O\text{-}CH\text{-}CHOH\text{-}CHOH\text{-}CHOH\ CH_2OH$$

and its close relationship to dextrose on the one hand and to cellulose on the other has been recently emphasized by various chemists, including the author.[2]

The data obtained by Pringsheim would appear to have an important bearing on the subject under discussion, since if it were possible to translate the same into commercial practice, in which any type of waste cellulosic material (vegetation, fibers, etc.) could be utilized, the problem of a future supply of liquid fuel would seem to be much nearer a solution.

It thus becomes possible, and permissible, to draw on the imagination and to visualize our future supply of liquid fuel as resulting from a direct conversion of the sun's rays through the medium of vegetation, the cellulose in which, under the influence of specific microörganisms is transformed first into cellobiose, secondly into glucose, and then into alcohol. This would mean the utilization of most of our waste fiber such as corn stalks, flax, waste wood, etc., by the cheapest and most economical of all processes, namely a combined saccharification-fermentation process brought about by the ceaseless activity of myriads of tiny microorganisms.

The apparatus would probably consist of a simple type of vat for conducting the fermentation of the ground cellulosic material, together with stills for the rectification of the alcohol.

This visualization of the important role to be played by alcohol in the future economic life of the nation points to the imperative necessity for the fostering of anything calculated to develop and maintain the manufacture of industrial alcohol at the highest point of efficiency. At the moment there is some danger that the recent brilliant accomplishments in this field, may, under the influence of pernicious and unenlightened legislation, be stultified to such an extent as not merely to cripple existing chemical industries, but to endanger our national standing and security, associated as it is so intimately with that of an adequate future supply of liquid fuel for transportation purposes.

SOURCES OTHER THAN ALCOHOL

While throughout this paper especial importance has been placed on the production of alcohol, the possibility of a cheap fuel from other sources of available raw material such, for example, as that of furfuraldehyde from corncobs should not be overlooked, and the interesting results of La Forge in this field are entitled to serious consideration, especially in view of the data submitted. According to this authority the corn waste (stalks and cobs) amounts to about 130,000,000 tons, capable of yielding 13,000,000 gallons of furfuraldehyde or a total of 3,900,000,000 gallons. In addition to this there is also obtained an immense quantity of cellulose which could be converted into alcohol. While the few experiments already carried out on the use of furfuraldehyde as a motor fuel apparently indicate its unsuitability on the ground of "pre-ignition" in the motor, it is not improbable, should the necessity arise, that this could be overcome.

There is also the question of the extensive deposits of shale awaiting suitable development for conversion into liquid fuel, and it may reasonably be expected that exploitation of these will take place in the not-too-distant future.

The important task for our domestic companies concerned with the production and marketing of gasoline, and faced with an impending shortage of their raw material in the near future, would seem to lie in intensive scientific research work in the fields of cellulose and plant chemistry on the one hand, and of bacteriology on the other.

It would be no small laurel in the crown of one of the two or three leading oil companies, to whose ingenuity, skill, and daring the present generation owes no small part of its everyday comfort, if within the next ten years they were able to announce the completion of the first commercial unit, in which pulped cellulosic material from any source could, under the action of sturdy microörganisms be converted with theoretical yield, first into sugar and then into alcohol. Failing the necessary interest on the part of the oil companies, perhaps that peculiarly American genius, Mr. Ford, might be induced to add to his industrial conquest of the "cheapest car," not only "cheap fertilizer" but also "cheap synthetic fuel," and in so doing increase still further the debt of gratitude on the part of the American public.

For the moment the solution outlined above is simply a "scientific dream" but wilder phantasies than this have proved capable of realization!

"Patient, intensive, scientific research" is the keynote the writer desires to leave as his closing phrase to those most interested in the solution of this fascinting problem.

The Bureau of Chemistry, United States Department of Agriculture has just completed a compilation of reports from the individual producers and consumers of naval stores for the 1920 producing season, which shows that 488,548 casks of gum spirits of turpentine, and 1,577,398 round barrels of gum rosin were made. There were on hand at the stills on March 31, 1921, the close of the 1920 season, 30,429 casks of spirits of turpentine and 327,055 round barrels of rosin. The following table shows the above data in comparison with that for the 1919

	Season 1920		Season 1919	
	Turps.	Rosin	Turps.	Rosin
Production from pine gum	488,548	1,577,398	366,000	1,237,000
Production from wood and still wastes	34,932	180,138	30,889	159,271
	March 31, 1921		Feb. 2, 1920	
Stocks on hand at stills, end of season	30,429	327,055	[illegible]	[illegible]
	Season 1920		Season 1919	
Stocks at wood distilling and rosin reclaiming plants end of calendar year	7,616	50,822	1,764	22,593
	March 31, 1921		Feb. 2, 1920	
Stocks in hands of consumers....	30,528	217,302	26,340	290,045
Stocks at ports and yards, primary southern ports	60,916	432,238	34,519	211,238
Eastern ports and distributing points	2,558	11,063	2,363	23,417
Central distributing points.......	10,364	35,567	14,558	28,574
Western distributing points......	848	275	2,734	717
Total	74,686	479,143	54,174	263,946
Total production	523,480	1,757,536	396,889	1,396,271
Exports, calendar year..........	189,168	652,023	213,442	677,662
Left for domestic uses...........	334,312	1,105,513	183,446	718,609

---

[1] Haworth and Hirst, J. CHEM. SOC., **119** (1921), 193.

[2] Pringsheim, LOC. CIT., 280; Hess, LOC. CIT., Karrer and Widmer, LOC. CIT., Heuser, "Lehrbuch der Cellulosechemie," 1921; Hibbert, LOC. CIT.

SOCIAL INDUSTRIAL RELATIONS

The Science of Human Engineering

By H. W. Jordan

Syracuse, N. Y.

Under the title, "Manhood of Humanity," the Polish engineer Alfred Korzybski has just issued a book on The Science of Human Engineering. E. P. Dutton & Co. are the publishers.

Korzybski's work, in conjunction with Professor Edwin G. Conklin's, "The Direction of Human Evolution," provides a solid foundation of eternal natural law upon which chemists and engineers can build a new, unique, social industrial structure which shall characterize industry of the twentieth century by scientific humanitarianism as industry of the nineteenth century was characterized by scientific materialism.

Robert B. Wolf, vice president of the American Society of Mechanical Engineers and a member of the Federated Engineers' Committee on Elimination of National Economic Waste says, "I consider Count Korzybski's discovery of man's place in the great life movement even more epoch-making than Newton's discovery of the law of gravitation. It will have a far greater effect upon the development of the human race."

And A. F. Sheldon, president of the International Rotary Club, writes, "In my judgment Korzybski's 'Manhood of Humanity' is potent with possibilities of being a mighty contributing factor in restoration of financial equilibrium and economic balance throughout the world and the bringing about of a status of justice to all parties concerned in industrial and commercial relationships, employee as well as employer."

Without further comment "The Manhood of Humanity" is commended to the earnest study of American chemists.

We are living in an age of swift social action. In England, the status of labor has advonced further toward effective political power in the past seven years than in the previous two centuries. In our own country, as well as in England, direct political power of women has grown more in the last decade than in all previous ages. And the Russian Revolution, of some five years' duration, marks the transition of the peoples of the eath from competitive, individualistic industrialism to cooperative, democratic industrialism; just as the French Revolution marked the passing of feudalism and the beginning of individualism.

The rapid transition will bring no greater disturbance than that which attends hurried installation of any improved process of manufacture, with erection of much new apparatus while keeping the plant in full operation ,if we be guided by the basic laws of evolution disclosed by Conklin and Korzybski. On the other hand, if we disregard these eternal laws and let ourselves be led by emotion and selfish, momentary expediency we will bury the social industrial world plant in a muddle of chaotic disorder.

If we remain content to let temporizing political leaders enact manmade laws, in utter disregard and defiance of laws of biological evolution, we will have "burned the barn to roast a pig."

Discussing the social industrial trend of 1921 and the rather ruthless regard of chemists and engineers by non-resident financial managers of great industries which the chemists and engineers have created by scientific research and applied science, a leading American engineer recently wrote, "The worst of the situation is that those responsible for it are not onscious of the fact that they are violating natural law. But natural law always works, regardless of whether we violate it consciously or unconsciously. To say, 'we didn't know it was hot, does not make the blister any less painful.'"

Chemists and engineers, collectively constitute the keystone of the social industrial structure. They stand between capital, executive management, and government regulation on the one hand, and labor, intellectual workers, and the public on the other. By their practical knowledge of science they rise head and sholders above either curve of the arch. They attained that preeminence through material science applied to industry.

To-day the keystone is in danger of disintegrating under the influence of corrosive seepage from active domination on the side of capital, and from crass indifference on the side of the public. The arch will collapse in ruin unless the keystone be protected by the acid resisting power of research applied to the Science of Human Engineering.

SCIENTIFIC SOCIETIES

The New York Meeting

This issue of the Journal is scheduled to reach our readers a day or two before the great rally of Anglo-Saxon chemists takes place in New York under the auspices of the American Chemical Society and the American Section of the Society of Chemical Industry. Doubtless, it will be the largest meeting approaching international proportions which has ever been held in this country. Our guests of the Society of Chemical Industry of Great Britain and its various Canadian sections will be receiving a welcoming hand in New York probably before they read these lines, yet, in order to be all-inclusive, a formal welcome to both, members of the American Chemical Society and their guests, from our own President Edgar Fahs Smith is published herewith:

A Message of Welcome and a Call to Duty from President E. F. Smith

Honored Guests and Fellow Members of the American Chemical Society:

You are aware that Chemistry is to-day much in the eye and on the tongue of every true, wide-awake American; hence it behooves us to make every effort to attend the meeting in New York, that we may hear subjects of vital importance discussed by thoughtful, far-sighted men. Through the fearful ordeal, visited upon it by the world war, our Country has learned the powers of the American chemist. To maintain the position won by him it is absolutely essential that chemists should foregather with their colleagues and participate in the meetings and advise on the various topics which will come before the

DR. MILTON L. HERSEY
Past Chairman, Canadian Section, S.C.I.

H. W. MATHESON, M.Sc., F.C.I.C.
Chairman, Montreal Section

DR. FREDERICK W. ATACK
Editor, "Chemists' Year Book"

CAPT. C. J. GOODWIN
Honorary Treasurer, Chemical Industry Club

MR. C. R. HAZEN
Chairman, Arrangements Committee, Canadian Meeting

DR. R. F. RUTTAN
Past President, Canadian Section, S.C.I.

E. V. EVANS, O.B.E., F.I.C.
Honorary Treasurer, Society of Chemical Industry

DR. J. P. LONGSTAFF
General Secretary, Society of Chemical Industry

Society in its several sections. Further, chemists should fraternize more than they have in the past. As far as possible we chemists must become a unit—learn to know one another more intimately.

In the several Bulletins, issued by sections during the year and which have been thoughtfully sent to my desk, I note the enthusiasm with which local interest is being developed but our main objective must continue to be a strong unified national viewpoint. This can be secured only by the opportunity of personal contact which our general meetings afford. Come, hear what your colleagues have to say.

Is there to be an American Chemistry?

This question surely will be answered affirmatively by all of us. That there may be no doubt make it a point to be in New York in September.

We are to have the privilege and pleasure of greating fellow chemists from the Dominion to the North and from beyond the seas. They are bringing worthwhile messages. Let them our love and enthusiasm for a common Science.

SIR WILLIAM J. POPE, D.Sc., F.R.S., K.B.E.
President, Society of Chemical Industry

These lines are hastily written—and only written—that you may know of my great desire to have you come out and let yourselves be seen. I shall be delighted, as always, to greet my brethren, who have so splendidly made chemistry come home to every man's business and bosom. If we hope to achieve success as a profession it devolves upon us to act unitedly.

The opportunity to make chemistry secure in America is now.

There is no exaggeration in declaring that the present is a very critical moment for chemistry and chemists in this Country.

Let us make this the best meeting the Society has ever enjoyed.

Faithfully yours,
(*Signed*) Edgar F. Smith.

PROGRAM OF THE MEETINGS

A general outline of the program and activities of the New York meeting was printed in the August issue of This Journal, but some of the main features and particularly the final details as nearly as they could be ascertained at the time of going to press are given below.

The program of the Society of Chemical Industry will have been completed at Montreal by September 1st. The committee in charge have outlined the following entertainment program for visiting members upon the completion of their trips to Ottawa, Toronto and Niagara following the meeting at Montreal:

Monday, September 5

Foreign guests will be met by a Committee from the American Section and conducted through industries on the American Side of the Falls. Luncheon at the Falls. Dinner at Buffalo. Special train of Sleeping Cars to Syracuse, N. Y.

Tuesday, September 6

The Solvay Process Company, Syracuse, N. Y., will entertain at luncheon and a tour through the great factory. Luggage will be left on the train which will not depart until mid-afternoon and will proceed to Albany, where we will take the night boat down the Hudson River to New York.

Wednesday, September 7

New York, 1:00 p. m.—Luncheon by the American Section to Foreign guests.
4:00 p. m.—Reception and tea to Foreign guests, and to Scientific Societies, at Columbia University.
8:00 p. m.—Smoker and Entertainment of American Chemical Society. (Foreign guests invited.)

Thursday, September 8

The usual general, divisional, and sectional meetings of the American Chemical Society, to which all foreign guests are cordially invited.

Friday, September 9

The usual general, divisional, and sectional meetings of the American Chemical Society, to which all foreign guests are cordially invited.

7:00 p. m.—Banquet of American Chemical Society.— Foreign guests welcome.

Saturday, September 10

Golf and tea.

Sunday, September 11

Boat trip and tea.

Monday, September 12 to Saturday, September 18

The National Exposition of Chemical Industries.

The regular business and scientific program of the American Chemical Society so far as known in detail at the time of going to press is as follows:

Tuesday, September 6

9:00 a. m.—Registration begins at The Chemists' Club, 52 East Forty-first Street.
3:00 p. m.—Council Meeting at The Chemists' Club, 52 East Forty-first Street.
6:30 p. m.—Dinner to the Council at The Chemists' Club, 52 East Forty-first Street.
6:30 p. m.—Dinner to wives of Councilors.
9:00 p. m.—Adjourned Meeting of Council, if necessary.

Wednesday, September 7

10:00 a. m.—General Meeting at Columbia University.
Address by Sir William Pope, D. Sc., F.R.S., K.B.E., President of the Society of Chemical Industry of Great Britain.
Address by Hon. Herbert Hoover, Secretary of Commerce of the U. S. A.
12:30 p. m.—Society of Chemical Industry Luncheon to British and Canadian visitors.
2:00 p. m.—Divisional Meetings at Columbia University.
4:00 p. m.—Reception and Lawn Party given by Columbia University.
8:00 p. m.—Smoker at Waldorf-Astoria Hotel.

Thursday, September 8

9:30 a. m.—Divisional Meetings at Columbia University.
2:00 p. m.—Divisional Meetinsg at Columbia University.
2:30 p. m.—Organ Recital at Great Hall, College of the City of New York, by Prof. Samuel A. Baldwin, Head, Department of Music.
3:00 p. m.—International Meeting at Great Hall, College of the City of New York, on "Chemistry and Civilization." (Dr. Edgar F. Smith in Chair.)
Science and Civilization; the Role of Chemistry. Charles Baskerville.
Energy; Its Sources and Future Possibilities. Arthur D. Little.
The Engineer; Human and Superior Direction of Power. Leo H. Baekeland.
Chemistry and Life. Sir William J. Pope.
Theories and Their Development. Willis R. Whitney.
Research Applied to the World's Work. C. E. K. Mees.
Problem of Diffusion and Its Bearing on Civilization. Ernst Cohen.
Catalysis, Directing Factors in all Changes. Wilder D. Bancroft.
8:00 p. m.—Banquet at Waldorf-Astoria Hotel.

Friday, September 9

9:30 a. m.—Divisional Meetings at Columbia University.
2:00 p. m.—Divisional Meetings at Columbia University.
8:00 p. m.—Public Meeting. President's Address.
Progress of Chemistry. Edgar Fahs Smith, American Chemical Society.

Saturday, September 10

Excursions.

CALENDAR OF MEETINGS — On Page Eleven — —

Calendar of Meetings

American Pharmaceutical Association—Sixth-ninth Annual Meeting, Hotel Grunewald, New Orleans, La., week of September 5, 1921.

American Chemical Society and Society of Chemical Industry—New York, N. Y., September 6 to 10, 1921.

Seventh National Exposition of Chemical Industries—Eighth Coast Artillery Armory, New York, N. Y., September 12 to 17, 1921.

American Institute of Mining and Metallurgical Engineers—Fall Meeting, Wilkes Barre, Pa., September 12 to 17, 1921.

American Electrochemical Society—Fall Meeting, Lake Placid, N. Y., September 29 to October 1, 1921.

Technical Association of the Pulp and Paper Industry—Fall Meeting, Washington, D. C., Philadelphia, Pa., Spring Grove, York, York Haven, Pa., and Wilmington, Del., October 18 to 20, 1921.

American Institute of Chemical Engineers — Annual Winter Meeting, Baltimore, Md., December 6 to 9, 1921.

SEVENTH NATIONAL EXPOSITION — On Galley 13 —

PROGRAM

Monday, September 12

2:00 p. m.—Exposition opens.
7:00 p. m.—Motion Pictures (In Auditorium):
1: "Iron Mining Operations." (4 reels) (Courtesy Bureau of Mines.)
  (*a*) Stripping.
  (*b*) Exploration and Stripping.
  (*c*) Underground Mining.
  (*d*) Logging Operations.
2: "The Jewels of Industry." (8 reels) (Courtesy, The Carborundum Company.)
  (*a*) Creating Power from Water.
  (*b*) Within the Power Plant at Niagara.
  (*c*) In and About the City of Niagara Falls.
  (*d*) Power at Work in the Carborundum Plant.
  (*e*) Making the Crystal Masses in the Electric Furnace.
  (*f*) And Making Them into Stones, Grinding Wheels, Paper and Cloth.
  (*g*) Unusual and Usual Uses for Abrasives in some Fifty Industries.
8:00 p. m.—Opening Addresses (Colonel's Reviewing Stand):
Opening Address by Chas. H. Herty.
Brig. Gen. Amos A. Fries, Chief, Chemical Warfare Service, U. S. A.

Tuesday, September 13

2:30 p. m.—Crushing, Grinding and Pulverizing Symposium.
Harry J. Wolf, *Chairman.*
"Ball and Pebble Milling for Pulverizing and Mixing," H. F. Kleinfeldt (Abbe Engineering Company).
"Grinding and Pulverizing with Air Separation," S. B. Kanowitz (Raymond Bros. Impact Pulverizer Company).
"Crushing, Storing and Pulverizing," L. H. Sturtevant (Sturtevant Mill Company).
"Dust Collection as Applied to Grinding and Pulverizing Problems," M. I. Dorfan (Allis-Chalmers Manufacturing Company).
"The Development of Compound Grinding Mills," H. Schifflin (Allis-Chalmers Manufacturing Company).
Industrial Problems Symposium
"Solvent Extraction of Edible Fats and Oils," H. Austin (Ernest Scott & Company).
"Materials Handling in Industrial Plants," R. H. McLain (General Electric Company).
"Utilization of Industrial Waste: Its Economic Importance," W. H. Dickerson (Industrial Waste Products Company).

To be followed by motion pictures upon the subject of the "*Handling of Materials*" if time permits. See the first six titles upon this evening's program.

7:00 P. M.—MOTION PICTURES:

1: "Use of the Steam Shovel in Mining." (1 reel) (Courtesy Bureau of Mines.)
2: "Transportation and Storage of Iron Ore." (1 reel) (Courtesy Bureau of Mines.)
3: "Transporting and Handling Coal by Various Means." (1 reel) (Courtesy Bureau of Mines.)
4: "Dredging Anthracite Coal." (1 reel) (Courtesy Bureau of Mines.)
5: "Saving Wasted Millions through Material Handling Equipment." (2 reels) (Courtesy Economy Engineering Company.)
6: "The Story of Sulfur." (2 reels) (Courtesy Texas Gulf Sulphur Company.)
7: "Mining and Extraction of Radium from Carnotite Ore." (2 reels) (Courtesy Bureau of Mines.)
8: "DuPont Dyes. Showing their Manufacture." (2 reels) (Courtesy E. I. duPont de Nemours & Company.)
9: "Making Soap." (1 reel) (Courtesy Baumer Films.)
10: "Mine Explosion and Rescue." (1 reel) (Courtesy Bureau of Mines.)

WEDNESDAY, SEPTEMBER 14

2:30 P. M.—EVAPORATING AND DRYING SYMPOSIUM.

Wallace Savage, *Chairman.*
(Subject to be announced.) E. G. Rippel (Buffalo Foundry & Machine Company).
"The Relation of Atmospheric Conditions to Chemical Processes," A. E. Stacy, Jr. (Carrier Engineering Corporation).
"Drying and Drying Problems," H. S. Landell (Proctor & Schwartz).
"Special Problems for Enameled Evaporators," Max Donauer (Elyria Enameled Products Company).
"Drying with Moist Air," Arthur B. Stonex (Hunter Dry Kiln Company).
"Drying as an Air Conditioning Problem," A. W. Lissauer (W. L. Fleisher & Company, Inc.).
"Atmospheric Drying by Means of Compartment, Tunnel and Continuous Belt Conveyor Dryers with some Practical Applications," J. D. Stein (Grinnell Company, Dryer Division).
"Spray Drying," W. H. Dickerson (Industrial Waste Products Company).
"Evaporation," H. Austin (Ernest Scott & Company).
"A New Arrangement of Heating Tubes in Heat Exchange Apparatus," Robert V. Cook (Chemical Equipment Company).
"A New Arrangement of Heating Tubes in Heat Exchange Apparatus," Robert V. Cook (Chemical Equipment Company).

7:00 P. M.—MOTION PICTURES:

1: "The Manufacture of Dry Sausage." (2 reels) (Courtesy Armour & Company.)
2: "The Making of Oleomargarine." (1 reel) (Courtesy Armour & Company.)
3: "The Electric Heart—The Dry Cell." (1 reel) (Courtesy Baumer Films.)
4: "Canning Electricity—The Wet Cell." (1 reel) (Courtesy Baumer Films.)
5: "The Manufacture of Pyrex Glassware." (3 reels) (Courtesy Corning Glass Company.)
6: "The Manufacture of Portland Cement." (2 reels) (Courtesy Bureau of Mines.)
7: "The Manufacture of Dynamite." (1 reel) (Courtesy Bureau of Mines.)
8: "Exterminate the Mosquito." (1 reel) (Courtesy Bureau of Mines.)

THURSDAY, SEPTEMBER 15 (PAINT AND VARNISH DAY)

2:00 P. M.—PAINT AND VARNISH SYMPOSIUM

R. S. Perry, *Chairman.*
"Paint and Varnish Waste Control," R. S. Perry (Perry & Webster, Inc.).
"Reflection Factors on Industrial Paints," H. A. Gardner (Institute of Paint & Varnish Research).
"Laboratory Control," L. P. Nemzck (E. I. duPont de Nemours & Company).
"Rust: Its Cause and Prevention," Maximilian Toch (Toch Brothers).
"Physical Testing of Paints and Paint Materials," Frank G. Breyer (New Jersey Zinc Company).
"The Ideal Paint and Varnish Specification," F. P. Ingalls (John W. Masury & Company).
"Limitations of Standardization of Paint and Varnish Manufacture," D. A. Kohr (Lowe Brothers Company).

7:00 P. M.—SAVE THE SURFACE.

"Save the Surface and You Save All with Paint and Varnish," Ernest T. Trigg (*Chairman*, "Save the Surface" Committee, Paint Manufacturers Association of the United States).
"What is Paint?" G. P. Heckel, (*Secretary*, Paint Manufacturers Association of the United States).

MOTION PICTURES:

1: "Making White Lead." (2 reels) (Courtesy Bureau of Commercial Economics and National Lead Company.)
2: "Making of Varnish." (1 reel) (Courtesy Bureau of Commercial Economics and Murphy Varnish Company.)
3: "Making of Paint and Varnish." (2 reels) (Courtesy Bureau of Commercial Economics and Sherwin-Williams Company.)
4: "Making of Paint." (1 reel) (Courtesy Bureau of Commercial Economics and Lowe Bros.)
5: "Making of Paint." (1 reel) (Courtesy Bureau of Commercial Economics and Mathews & Company.)
6: "Making of Varnish." (1 reel) (Courtesy Bureau of Commercial Economics and Taylor, Tregent & Company.)
7: "The Manufacture of Pyrex Glassware." (3 reels) (Courtesy Corning Glass Company.)
8: "The Manufacture of Portland Cement." (2 reels) (Courtesy Bureau of Mines.)

FRIDAY, SEPTEMBER 16

2:30 P. M.—THE POWER PLANT IN THE CHEMICAL INDUSTRIES SYMPOSIUM

R. C. Beadle, Editor *Combustion, Chairman.*
"Modern Boiler House Arrangement and Equipment" (Illustrated), R. M. Gordon (The Solvay Process Company).
"Suggestions for Reducing Heat Losses in Chemical Plants," John Primrose (Power Specialty Company).
"Boiler Feed Water Treatment and Treatment Control," E. G. Bashore (Rice & Bashore).
"Compressed Air Installations in Industrial Plants," A. R. Stevenson, Jr. (General Electric Company).
"The Application of Electric Power in Chemical Industry," D. B. Rushmore, J. A. Seede, and E. Pragst (General Electric Company).
"The Limitation of Silent Chain Drive," F. G. Anderson (Morse Chain Company).
"A New Method for Coking Coal as Required for Industrial Fuel," D. S. Chamberlin (Distillation Industries, Inc.).
"The Application of Pulverized Fuel," H. D. Savage (Combustion Engineering Company.)

To be followed by Motion Pictures upon *The Power Plant* if time permits. See the first four titles upon this evening's program.

7:00 P. M.—MOTION PICTURES:

1: "The Cost of Careless Firing." (2 reels) (Courtesy Bureau of Mines.)
2: "Getting the Most out of Coal." (1 reel) (Courtesy Bureau of Mines.)
3: "Conserving Coal and Saving Heat Values by Insulating Steam Pipes and Boilers." (1 reel) (Courtesy Magnesia Association of America.)
4: "Modern By-Product Coking." (2 reels) (Courtesy The Koppers Company.)
5: "The Story of Rock Drilling." (4 reels) (Courtesy Sullivan Machinery Company and Bureau of Mines.)
6: "The Story of Armco Ingot Iron." (3 reels) (Courtesy American Rolling Mill Company.)

SATURDAY, SEPTEMBER 17

2:30 P. M.—AMERICAN DYES:

Justin B. Weddell, National Aniline & Chemical Company, *Chairman.*

7:00 P.M. MOTION PICTURES (subject to change):

1: "Zinc Mining, Milling and Smelting." (4 reels) (Courtesy Bureau of Mines.)
2: "Manufacture of Zinc Oxide." (1 reel) (Courtesy Bureau of Mines.)
3: "Making duPont Dyes." (2 reels) (Courtesy E. I. duPont de Nemours & Company.)
4: "Manufacture of Dynamite." (1 reel) (Courtesy Bureau of Mines.)
5: "Mining Magnetic Iron Ore." (2 reels) (Courtesy Bureau of Mines.)

NOTES AND CORRESPONDENCE

The Detection of Phenols in Water

Editor of The Journal of Industrial and Engineering Chemistry:

By reason of familiarity and former connection with certain trade waste investigations relating to water supplies in Western Pennsylvania, the writer takes the liberty of offering a correction to the above paper by Mr. R. D. Scott in the May issue of THIS JOURNAL, 13 (1921), 422.

Credit for the adaptation of the Folin-Denis reagent (phosphotungstic, phosphomolybdic acid) to water examination belongs to Mr. E. P. Fager who, prior to January 1920, was chemist in charge of the filtration plant of the South Pittsburgh Water Company, Pittsburgh, Pa. During the early part of 1919 some water supplies on the lower Monongahela River, particularly the McKeesport and South Pittsburgh plants, experienced considerable complaint on account of disagreeable taste and odor due to phenol wastes from chemical plants upstream. Following the South Pittsburgh experience Mr. Fager was assigned the problem of detecting and identifying this class of waste and succeeded in developing several methods suitable for the purpose, of which the Folin-Denis adaptation seemed the most promising. In the winter of 1919 to 1920 practical application of the method was made in studying the trade waste problems of the New Castle works, which are under the same management; namely, The American Water Works & Electric Company of New York. In the New Castle studies the direct colorimetric method was improved by the distillation method to avoid interference due to other impurities.

In tracing what is believed to be the first use of the Folin-Denis test for phenols in water supplies, the writer in nowise disparages the subsequent excellent work done by Mr. Trowbridge at the New Castle works. So far as the writer is aware, this is the only waterworks in the country where an effort has been made systematically to record quantitatively the phenols present in a public water supply, the toleration by consumers after chlorination, and the reductions feasible with a rapid sand filter plant. The writer is cognizant of the painstaking investigations at Milwaukee in correlating the phenol pollution with the occurrence of taste and odors in the water supply and wishes to acknowledge the great value to the waterworks fraternity, and chemical industries as well, of the published conclusions (*Eng. News-Record*, 82, 181; 84, 1155), first calling attention to the aggravated effects of this class of wastes in chlorinated supplies.

Mr. Scott is somewhat inaccurate in stating that the detection of phenols in water rests upon the Folin-Denis test. It is nearer the truth to state that the method is probably the most convenient of several methods available, especially for field work. As a matter of fact, the literature shows many more interfering substances than those mentioned by the author. In any careful investigation of phenols in a water supply, proper precautions should be taken to establish the specificity for the local problem, and should preferably include differentia of the very large group of phenolic compounds liable to occur as polluting substances. With proper precautions, and using the distillation method, it may be said that the Folin-Denis test gives the water analyst a method which closely approximates the free and albuminoid ammonia determinations in sensitiveness.

WELLINGTON DONALDSON

FULLER & MCCLINTOCK
170 BROADWAY, NEW YORK, N. Y.
June 11, 1921

. .

Editor of The Journal of Industrial and Engineering Chemistry:

Reference was made by Mr. Scott in his article to my experiments at the filtration plant in New Castle, Pa., on the detection of phenols in water, without a knowledge of the extent or the facts concerning the work that has been done by Mr. Donaldson, Mr. E. P. Fager, and myself. Mr. Donaldson is correct in stating that credit for the adaptation of the Folin-Denis reagent to water examination belongs to Mr. E. P. Fager.

When Mr. Fager was in charge of the filtration plant of South Pittsburgh Water Company, I had access to the results of his experiments and later used them, in connection with my investigation at New Castle, Pa.

I appreciate the value of the application of the phosphotungstic phosphomolybdic acid reagent for the detection of minute quantities of phenol wastes in water, and I shall be very grateful if Mr. Donaldson's correction is published.

Mr. Scott has pointed out that the reagent is not specific for phenols and has named some of the substances which may effect the determination. In our work, we were entirely familiar with the limitations of the test.

CHARLES E. TROWBRIDGE

AMERICAN WATER WORKS & ELECTRIC CO., INC.
50 BROAD ST., NEW YORK, N. Y.
June 18, 1921

. .

Editor of The Journal of Industrial and Engineering Chemistry:

I am grateful for the correction which Mr. Donaldson offers, for it appears from his comment that Mr. E. P. Fager, rather than Mr. Trowbridge, first applied the Folin-Denis test for phenols in water examination. Although it appears further in Mr. Fager's study that "the direct colorimetric method was improved by the distillation method to avoid interference due to other impurities," it would seem that this modification was not employed by Mr. Trowbridge at New Castle since no mention was made in a personal communication from him of any method other than the direct colorimetric. The distillation method was adopted by us solely on the basis of our own experience.

With respect to the implication of inaccuracy in the writer's statement that the detection of phenols in water rests upon the Folin-Denis test, it would perhaps be well to emphasize again the fact that the detection of traces of phenol cannot be accomplished satisfactorily by any of the other methods described in the literature, for after careful trial of these it was found that none except the Folin-Denis was reliable in detecting amounts of one part per million or less. Amounts higher than this would rarely be found in a public water supply. In this connection it is interesting to note that in the work at Milwaukee, to which Mr. Donaldson refers, the phenol determination did not rest upon a definite quantitative chemical test but upon the chemist's sense of taste and smell after chlorinating a water suspected of containing phenols. One of the prime factors promoting the study of this problem and influencing us in publishing our results was the fact that the chemist who had charge of the Milwaukee studies encountered similar conditions at Cleveland and was at a loss for a definite method for determining phenols in water. It was deemed inadvisable to include in the original article a discussion of this and similar points, since an attempt was made to outline briefly only the essential points in connection with the test from the laboratory standpoint. For this reason also a detailed discussion of the various substances which respond to the Folin-Denis test was not presented.

In our opinion it would be a somewhat hopeless task to attempt, as suggested by Mr. Donaldson, any differentiation of the large group of phenolic compounds likely to be found in waters. It would be much more promising to make a study of the wastes from individual establishments before such materials enter a water supply. This, of course, is a subject not considered in the article under discussion.

R. D. SCOTT

STATE DEPARTMENT OF HEALTH
COLUMBUS, OHIO
July 5, 1921

Assignment of Patents

Editor of the Journal of Industrial and Engineering Chemistry:

The findings of fact and law in the action by Air Reduction Co., Inc., against Warren R. Walker, to which reference is made in the July issue of the JOURNAL, will perhaps leave your readers in doubt as to the governing principle of the decision.

The action was brought to compel assignment by Walker to the Company of an application for Letters Patent covering an invention made jointly by Walker with Floyd J. Metzger and involves the right of the employer to inventions made by an employee. This right has been the subject of numerous controversies and, in the absence of express agreement, depends upon the character of the employment. Walker's relation to his employer in this case is stated in the decision of Mr. Justice Cropsey, from which the following is quoted:

> There was no express agreement making any invention of the defendant the property of the plaintiff, nor was there any express agreement that the defendant would assign to the plaintiff any patent he might obtain. But he was employed to give his time and scientific skill for the very purpose of trying to discover and invent some practical use for this gas. In other words, he sold his inventive powers to the plaintiff during the period of his employment. Under these circumstances I think there is an implied agreement that the results of defendant's work shall belong to plaintiff and that any patent obtained by defendant should be assigned by him (Annin v. Wren, 44 Hun, 352; Connelly Mfg. Co. v. Wattles, 49 N. J. Eq., 92; Meissner v. Standard Railway Equipment Co., 190 S. W. Rep., 730; Supreme Court of Missouri; Dowse v. Federal Rubber Co., 254 Fed. Rep. 308; Famous Players-Lasky Corporation v. Ewing, 194 Pac. Rep. 65, Cal.). No case in this state holding the contrary has been brought to the Court's attention. Clark v. Fernoline Chemical Co. (5 Supp., 190) decides only a question of pleading. Its statements upon this subject are purely *obiter*. There are decisions in some other jurisdictions which seem to be at variance with those above cited (see American Circular Loom Co. v. Wilson, 198 Mass., 182, 201; Dalzell v. Dueber Mfg. Co., 149 U. S., 315; Barber v. National Carbon Co., 129 Fed. Rep., 370; Pressed Steel Car Co. v. Hansen, 137 Fed. Rep., 403; Hildreth v. Duff, 143 Fed. Rep., 139; Hapgood v. Hewitt, 119 U. S., 226). Some of these cases may be distinguishable, but even if they be not, I believe the sounder rule is set forth in the cases first cited. Hence the plaintiff is not entitled only to a shop right to use the patent, but is entitled to own it outright, and hence should have judgment against the defendant, with costs.

It may also be of interest to note the language of Mr. Justice Pratt in Annin v. Wren, 44 Hun, 352, which is as follows:

> The special service of *inventing* under special *employment to invent* gives the master the servant's inventions which result from that service. (Simonds Manual of Patent Law (Ed. 1883) pp. 202-204). This is also the principle of that part of the decision of Burr v. DeLaVergne (102 N. Y. 415), which relates to the inventions made by DeLaVergne alone. The same is true of Binney v. Annan (9 Am. Rep. 10; 107 Mass. 94). None of the patent cases are inconsistent with the principles above indicated. Even in Hapgood v. Hewitt (11 Fed. Rep. 422), lately affirmed (110 Fed. Rep. 227), Judge Gresham excepts the case of a special employment *to invent*. The special service of inventing is the entire scope of the employment. There is no room left within the employment for inventing on his own hook. The servant has no right to think or invent for himself on this particular subject matter in hand. He must get out of such a relation before he can claim the product of his work under such an employment. He cannot carry off both his salary and the only valuable product of his work under such an employment, leaving his master with his useless models, the result of his uselessly spent money on tools, machinery, time, labor of self and employees with only a license or shop right, which is not assignable or useful in any way than to himself.

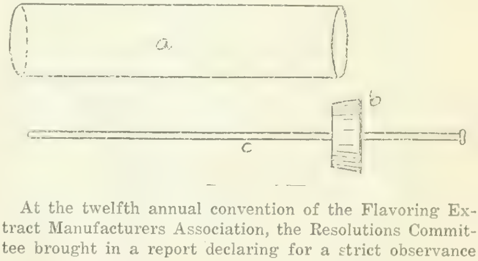
The foregoing will serve to indicate quite clearly the relation of employer and employee with respect to inventions, where the employee is engaged in research or is employed for the purpose of making inventions.

E. H. MERCHANT

AIR REDUCTION CO., INC.
342 MADISON AVE., NEW YORK CITY
August 3, 1921

A Study on the Oil Bromide Test of Linseed Oil

This drawing was inadvertently omitted from its proper position in column 1, page 802, of this issue.



At the twelfth annual convention of the Flavoring Extract Manufacturers Association, the Resolutions Committee brought in a report declaring for a strict observance of all provisions in the prohibition amendment. This recommendation, together with an agreement binding members of the association in a war against unscrupulous extract manufacturers, was adopted unanimously. It was also agreed that the flavoring extract men should instruct the Research Committee to continue its efforts to find a substitute for alcohol. At the executive session, the association pledged itself to force certain manufacturers who are not members of the association, and who are evading the Volstead law, out of the business.

WASHINGTON LETTER

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

THE TARIFF BILL

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

The tariff bill has spent an eventful month in Congress. After the discussion in the House, the bill was passed on to the Senate without the dyes embargo provision. The bill itself passed the lower chamber by a substantial majority, but the provisions protecting the American dye industry for three years were thrown out by only a few votes.

The action of the House was a surprise, and it precipitated a bitter and lively fight, for and against the embargo, at the hearings that have just been held by the Senate finance committee. What the final fate of the dyes embargo will be is known only by Senator Penrose and his committee, if they have made up their minds.

Meanwhile, the three months' lease on life given to the licensing system for control of dyes imports by the emergency tariff law has been fleeting away. It would expire on August 27, and would allow a flooding of American markets with dyes that would supply our needs of months and ruin the industry. This danger was foreseen by those who have been fighting for the chemical industry in Congress, and Representative Longworth has introduced a bill providing for the extension of the licensing system for three months longer. Under the urge that was provided by a letter from President Harding, stating "we would be both unmindful and unjust if we failed in a suitable protection of this country until the new and complete tariff revision act is made effective," the House to-day passed the extending bill and prompt action on the part of the Senate is expected to complete the extension of time.

Representative Young has just introduced a bill to extend the life of the emergency tariff act itself for two months from November 27 and this is taken to indicate that it will not be until the end of this year at least that the regular tariff is placed on the statute books. If this is the case, it is probable that even further extension of the life of the dyes licensing feature than that provided in the Longworth bill will have to be secured later.

SENATE FINANCE COMMITTEE HEARINGS ON DYE EMBARGO

It is reported currently that the Senate Finance Committee has virtually decided to retain the American valuation provision of the tariff bill, probably slightly modified. This is of interest to the chemical industries, as American valuation will in effect mean higher duties on imported chemicals. The Senate Finance Committee is now considering the valuation and dyes features of the tariff bill behind closed doors with only the Republican members of the Committee present.

The Finance Committee hearing from a chemical standpoint centered largely in the testimony about the dyes embargo provisions, although two days were spent previously on Schedule 1 on chemicals, oils, and paints.

Brig. Gen. Amos A. Fries, chief of the Chemical Warfare Service, appeared before the Committee and told them how the gas warfare material and the explosives used in war are produced from practically the same materials as dyes. With no embargo protection, the American dye industry would be killed by a flood of German dyes, and this would destroy the military safeguard that those chemical plants are to this country. During the questioning of General Fries, he was asked whether he thought that disarmament among the nations would not have as one of its chief results the abolition of gas, and he brought out the fact that gas is the only kind of armament that would cost us very little in times of peace. Dye plants could be turned into poison gas plants in time of war, and, with a proper development of the coal-tar industry, this country could keep up to date in gas warfare easily and at little cost, he said. Admiral W. Strother Smith of the Navy also declared that the embargo or some other dye protection was necessary as a military measure.

Herman A. Metz, president of the Consolidated Color and Chemical Co., of Newark, N. J., was the principal witness against the embargo, who testified at length. Jos. H. Choate, representing the American Dyes Institute, presented the side of the dye manufacturers and declared that America was up against a most unscrupulous competitor in the commercial world, in referring to Germany's dye industry. Throughout the hearings, there were continual verbal encounters between these two men.

Among those who appeared in favor of the embargo were: Charles H. Stone, vice president of the Atlantic Dyestuff Co.; Gaston Du Bois, president of the Monsanto Chemical Works; W. Parker Jones, representing the Victor Chemical Works, Chicago; S. Isermann, representing the Chemical Company of America; B. T. Bush, representing the Antoine Chiris Co.; Henry B. Thompson, president of the United States Finishing Corporation, and Dr. Marston Taylor Bogert, professor of organic chemistry at Columbia University. Among those who opposed the embargo were: Granville MacFarland, representing the Amoskeag Manufacturing Co.; William H. Brehm, of Brehm and Stehle, and C. B. Reid, representing the American Farm Bureau Federation. The Senate Finance Committee is headed by Senator Penrose, who presided at the hearings.

The hearings involved the Chemical Foundation, and the charges that had been made previously by Representative Frear and Senator King that the Chemical Foundation seized alien patents and that it was engaged in a "pernicious dye lobby" were aired, principally in the examination of Mr. Choate and Mr. Metz.

The dye embargo was aided when Senator Penrose recently made public letters from Secretary Weeks and Denby declaring that the military safety of the country depends to a great degree upon the dye embargo.

THE PROHIBITION BILL

The prohibition bill that had been drawn in the House so that it endangered the industrial and chemical alcohol production has been radically amended and passed by the Senate. When it was being sent to conference in the House, however, it hit a snag in the way of another amendment, and it now seems that it will not be acted upon until October. On the floor of the Senate, objections to the pending bill were raised by Senators Broussard of Louisiana, Stanley of Kentucky, and Brandegee of Connecticut, on the ground that it allows arbitrary changes of the formula of proprietary compounds. The manufacturers have declared, however, that the amended bill suits them.

Present plans provide for a month's recess by Congress beginning about August 20, and this is expected to provide a legislative breathing spell.

The House Ways and Means Committee is now engaged in framing tax legislation.

The bill affording relief for the patent office has made little further progress in Congress, while the applicants offering new inventions and demanding action on their claims have flooded the Patent Office. All previous records have been broken by the number of applications filed in the last six months, and there are now 51,865 patents awaiting action.

The Muscle Shoals Nitrate Plant

The Government had arrived at no decision as to whether the Ford proposal for the Muscle Shoals nitrate plant and dam will be accepted. The bid has been submitted to the Chief of Engineers, and Maj. Gen. Beach has recommended that it be accepted. This recommendation and his analysis of the proposition have been attacked by experts, according to press reports current here, on the ground that the proposal fails to cover the cost of the dams and that additional water storage at high cost would have to be provided by the Government. It has also been announced that several groups of financiers, including the du Pont interests, have submitted proposals, but these cannot compete with the Ford offer, it is said. The Alabama Power Company, said to represent powerful New York banking interests, will also submit a bid that will compete with Ford's, according to current reports.

DEPARTMENT OF COMMERCE CONFERENCE

Industrial trade and technical organizations were called into conference with bureau chiefs of the Department of Commerce last week for the purpose of getting advice as to the kind and amount of governmental statistics in industry that should be gathered and compiled in the biennial census next year.

Many suggestions were made and accepted, as a result of which the department will make further report on the probable changes.

A number of changes in the specifications used by the Government for the purchase of gasoline, kerosene, fuel and lubricating oil, were recently proposed at an open meeting of the Technical Committee on Standardization of Petroleum Specifications held under the chairmanship of N. A. C. Smith of the Bureau of Mines.

The Bureau of Mines is beginning research work on the coke that can be used in blast furnaces for fuel. This work will be undertaken in the Birmingham, Ala., district.

It is believed here that the Chemical Warfare Service of the Army should have not less than $4,000,000 next year to insure the proper development of this arm of the service.

Many Washington chemists are looking forward to a relief from their regular work next month when they go to New York to attend the meetings of the AMERICAN CHEMICAL SOCIETY and to see the Chemical Exposition.

AUGUST 11, 1921.

LONDON LETTER

By STEPHEN MIALL, 28, Belsize Grove, Hampstead, N.W.3, England

I think it was Lord Rosebery who said "There are two occasions when men make speeches, one, when they have something to say, the other, when they have to say something." I feel the truth of this observation very acutely; a letter on developments in industrial chemistry must be written. The heat and the drought do not promote a nimbleness of the mind; I have wandered up and down my parched little garden trying to think of the chemical developments which I well know are not taking place. It occurred to me to speak of the Synthetic Ammonia plant now being erected by Messrs. Brunner, Mond & Co. at Billingham, but it will be a year or a couple of years before it is turning out its several tons a day and many changes may have to be made in the interim.

This opportunity of an iteresting piece of news having been eliminated, the task still remains to be done, or perhaps begun. Then the historical method seemed possible and I commenced "On this day exactly one hundred and forty-seven years ago Priestley discovered oxygen," but the prospect of a history of oxygen and its developments to date filled me with dismay. Priestley made a greater discovery: soda-water, two words, as Webster said, connected by a syphon. This presented possibilities, but a liter of practice is worth a couple of pages of precept and I turned to the better course. Being still gravelled for want of matter—what fool was it who spoke of the indestructibility of matter?—I again stirred up the gruel I seem to have in place of cerebellum:

"It's easy to bid one rack one's brain—
I'm sure my poor head aches again,
I've scratched it so, and all in vain."

Thrice, and even four times, blessed are those who will travel to America in the flesh, who can meet their colleagues face to face, sharpen their wits on each other and expound their views on the philosophy of life and the deceitfulness of riches without having the agony of seeing their feeble phrases (or is it frases in the U. S. A.?) in cold print a month aftewards. But one must be careful how one jests on a matter of spelling. When you first spelt sulfur with an "f" Professor H. E. Armstrong rashly stated that we ought to withdraw our Ambassador from Washington, whereupon eleven chemists, of whom nine were Scotsmen, solemnly explained that spelling was not the concern of the diplomatic service and that to withdraw our Ambassador seemed an extreme measure to take even for so outrageous a breach of decorum.

Industrial Chemistry and the League of Nations seem far removed, but the latter has an International Labour Office and this a Health Section which deals with questions of industrial hygiene. The International Labour Office will meet in Geneva next October and has put forward a proposal to prohibit the use of lead compounds in painting. All the chemists concerned in lead or zinc mining or smelting, in the paint and varnish industry, and in allied occupations are busy with propaganda on one side or the other while medical men men and factory inspectors talk learnedly of arteriosclerosis and statisticians scrawl hieroglyphics alarming. Some facts seem to emerge from the fog of controversy and are, as yet, not sufficiently appreciated by chemical manufacturers; to begin with, the vapors of benzene, petroleum, turpentine and volatile thinners seem to be much more injurious than is commonly supposed. This point has been alluded to both in America and England before, but recent work by Sir Kenneth Goadby and others shows that there is a considerable danger to health from this cause. Another fact is that prevention of dust is the same thing as the prevention of disease, not only in the paint trade but in almost every occupation, farming only excepted. In some experiments on the detection of very small quantities of lead, Mr. C. A. Klein was for a while puzzled by dark stains when almost any solution was sufficiently concentrated, filtered, and treated with ammonium sulfite. Finally he proved that all filter papers are liable to contain copper in sufficient quantity to produce the necessary reaction, and it seems that the drying of the paper on bronze rollers or gauzes introduces this disturbing factor. In some cases the microscope reveals a dendritic growth of copper compound, and in exceptional cases the phenomenon is very marked.

What is research and how can it be promoted in the domain of industrial chemistry? Dr. Messel by his will left to the Society of Chemical Industry a sum exceeding £20,000 as an absolute gift but with the expression of a hope that it might be available for such an object. We are now trying to devise some scheme which will be worthy of this generous gift, and many are the suggestions which reach our Treasurer. While he considers the relative merits of medals, lectureships and scholarships and reads up the latest decisions on Charitable Trusts he steadily invests the income and I strongly suspect that he is mercenary enough to continue this practice until public opinion rises in its majesty and compels him to spend some money—well or foolishly—to justify his existence. A century or so ago a thrifty Englishman, named Thellusson, left a large sum of money to be accumulated until it would pay off our National Debt. Whenever I receive one of those persuasive forms appealing for income tax I curse the folly of the maniacs who prevented Mr. Thellusson's scheme from realization. And now I cry "Hands off Mr. Evans." He knows with Mr. Jingle that though there is a great deal to be done with fifty pounds, there is more to be done with a hundred and fifty. After all there are only two things which chemists should pursue, truth and money. Industrial chemists desire truth because it brings more money; pure chemists desire money because it enables them to attain more truth. How to blend the two; to discover the golden mean? This is the real problem, and the quadrature of the circle and the trisection of the angle are nothing to it. Chemical equations are sometimes reversible, and I am hoping that a state of equilibrium will in time be reached between the reagents of truth and money. But Treasurers seldom attain to this state, they rise in the morning repeating "Take the cash and let the credit go," and they go to bed murmuring "A fool and his money are soon parted." I was once a Treasurer myself.

August 1, 1921.

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France.

The French government is at present making a study of the better utilization of coal and lignite.

The prospecting for petroleum, which I have already discussed, does not seem to have given the hoped-for results. Therefore, search is being made for a solution of the fuel problem along some other line. It is desired to produce what is known as the "national carburetant," a mixture of different hydrocarbons and alcohol, especially benzene and ethyl alcohol, each in the proportion of 33 per cent.

A competition has been instituted by the Agricultural Society of the Department of the Herault, which specifies that the mixture shall contain amounts of alcohol varying between 10 and 50 per cent, to be used with motors of the prevailing type or with modifications, these motors being devoted to motor culture, agricultural industries, motor vehicles, navigation, or aviation. If any American chemist or company is interested in this competition, I can send him the announcement.

Along this same line, distillation tests carried out on 100 tons of lignite have given the following yield per ton of lignite:

25 kg. benzene
25 kg. paraffin
25 kg. ammonium sulfate

Although the United States is very rich in coal and petroleum, it is not neglecting lignite distillation, and is utilizing to the full the by-products of the coal. In France, at the present time, many small gas-works are not recovering their by-products, but a law, passed at the end of June, now obliges the gas-works to remove benzene, and also authorizes them to increase the proportion of water gas. A quantity of 15 or 18 per cent in illuminating gas has been pronounced inoffensive by the Conseil Superieur d'Hygiene. It is estimated that the application of this law, which, of course, substitutes coke for coal for the manufacture of the water gas, will reduce imports of coal by a million tons per year. On the other hand, considering all the gas-works, it is estimated that the benzene production will be from 25,000 to 30,000 tons per year. Further, the calorific value has been fixed at a maximum of 4700 calories and a minimum of 3500 calories.

THE HABER AND CLAUDE PROCESSES

The members of the committee appointed to estimate the comparative value of the Haber and Claude processes are not giving out the results of their investigation, and although the report has been submitted it is very difficult to find out what its conclusion was. French chemists are unanimous in deploring the fact that the private interests of the companies make such precautions necessary. There are involved here questions of a purely scientific sort, to which should be given the greatest possible publicity.

All one can say at present, from certain indications and with reservations, is that the committee has not pronounced itself clearly in favor of one or the other of the two processes. They seem to be equivalent, and the economy which would result from one or the other is of small value on account of the fact that the same difficulty exists in either case, that is, the cost of pure hydrogen. According to different engineers, it appears that this question of nitrogen needs to be studied in the industrial laboratory for some time longer.

HYDROGENATION OF FISH OILS

Following the example set in the United States, more and more research is being directed toward the utilization of sea products.

Mr. Marcelet has just been studying the hydrogenation of fish oil. It was already known that hydrogenation removes the odor which has made the oil unusable. Mr. Marcelet has been able to follow the lowering of the iodine number and the elevation of the melting pint, and to draw from this practical conclusions as to the utilization of the oil from the point of view of foods.

THE UNITED STATES TARIFF

A certain excitement has been manifested in France at the announcement of the appearance of the new United States customs tariff. The Chamber of Commerce of Paris, the president of which, Mr. Pascalis, is a manufacturer of chemical products, has issued a protest, based on the fact that the application of this tariff would necessitate annoying inquisitorial measures in French factories on the part of American tariff agents, and by a natural recoil American banks which have interests in Paris would have to expect to lose part of their clients.

The explanations from various sides which have appeared in the press reduce the apprehension to its true value. The list of substances admitted free to the United States is still relatively important, and it appears that the protective system adopted applies especially to the dyestuff industry, and is in a way legitimate on account of the considerable effort which is being made in this field in the United States, an effort which evidently needs a certain protection, at least for some years to come.

August 1, 1921.

Laboratory Fire at Tulane University

Fire which resulted in damage to equipment of approximately $20,000 and to the building of about $28,000 was discovered in the attic of the Richardson Chemistry Building, Tulane University, New Orleans, on the morning of July 6. No cause has been determined as to the origin of the fire. The top story of the building was completely destroyed, the second floor badly damaged, and the equipment on the main floor was damaged by water.

An interesting observation in connection with the fire is that "two shelves in theattic, which had been treated 10 years ago with aniline hydrochloride and copper sulfate were not even scorched although brass melted within three feet of them, and they were within 10 feet of where the fire is supposed to have originated."

Reconstruction has already commenced and it is hoped that the building will be back in shape in time for the opening of the fall term.

The latest report of the British Alkali Committee, which covers developments during 1920, outlines the present status of the industry as follows: During the year the number of registered chemical works was 1383; of these, 58 were registered as "alkali works," that is to say, works in which salt is decomposed with evolution of muriatic acid. There has been a decrease of four in the number of alkali works registered and of 16 in the number of other works, a total reduction of 20. The number of works by no means indicates the number of processes under inspection, as many works are registered for more than one process; in some instances the number of registerable processes in one works is as high as 10.

INDUSTRIAL NOTE

The Dye and Chemical Control Section of the Customs Service has prepared the following statement showing the commodities which are regarded as synthetic chemicals or drugs, and which therefore require special license for release from customs custody under the terms of the Emergency Tariff Act, also those which are not so considered. **Synthetic Organic Chemicals:** Formic, lactic, oxalic, pyrogallic, acetic, and valerianic acids, and all salts of the above, acetic anhydride, acetone, acetone oil, formaldehyde, chloral hydrate, urea, dionin (ethyl morphine), terpin hydrate, carbon tetrachloride, chloroform, cellulose esters, amyl acetate, amyl nitrite, ethyl acetate, ethyl chloride, sulfuric ether, butyl alcohol, iodoform, heroin, peronin, calcium cacodylate, mercury cacodylate. **Not Synthetic Organic Chemicals:** Citric, gallic, tannic, tartaric, prussic and glycerophosphoric acids, all metallic or inorganic radical salts of the above, thymol, glycerol, calcium cyanamide, sulfocyanides of metals or inorganic radicals, cocaine, morphine, caffeine, menthol, bismuth albuminate.

The French Academy of Sciences has just received a gift of 10,000,000 francs from Baron Edmond de Rothschild for use in research work.

The Baltimore and Ohio Railroad Company has reestablished its agricultural bureau to carry out the program begun in 1916 which was abandoned later on account of war conditions. The bureau is a part of the commercial development department, under the charge of Mr. H. O. Hartzell.

The United Indigo & Chemical Co., Ltd., a British corporation with offices in Boston, is required by a recent order of the Federal Trade Commission to refrain from certain competitive methods in the chemical industry. Testimony was given at the trial that during the three-year period, 1916, 1917, 1918, the United Indigo & Chemical Co., Ltd., expended for entertainment and gratuities to employees of its customers and competitors' customers an average of from $40,000 to $50,000 per year. These gifts were found to have been given without the knowledge or consent of the employers whose employees received the goods. This practice has been declared by the commissioners an unfair method of commerce, and its discontinuance ordered.

Fire damaged the Archer-Daniels Linseed Company's plant, at Buffalo, N. Y., recently. The fire was caused by spontaneous combustion, and resulted in a loss of $50,000.

The Maryland Vegetable Co., capital $1,250,000, has purchased the factory property of the Cocoanut Products Corporation, Baltimore, against which foreclosure proceedings have been instituted.

The American Society for Testing Materials has appointed a committee to work in conjunction with the Zinc Institute in testing zinc ores. The committee is headed by W. H. Bassett.

The American Chemical-Machinery Co., Philadelphia, has been incorporated in Delaware with a capital of $500,000.

PERSONAL NOTES

Major General W. L. Sibert, former head of the Chemical Warfare Service during the World War, is now back home on his farm in Warren County, Kentucky, where he is in the crude oil producing industry. Twenty wells are now going on General Sibert's land and one of these is credited with being the largest producer ever struck in Warren County.

Dr. Reuben S. Tour, government chemical expert, has been appointed professor of chemical engineering at the University of Cincinnati. Dr. Tour, who succeeds **Dr. O. R. Sweeney**, who resigned because of ill health, has served for several years as an expert for the government on nitrate and other chemicals, and will continue to act as consulting expert for the government. He had been offered, but refused, a position as chemical expert by a nation of Europe. Dr. Tour's new duties will begin September 1.

Dr. J. M. Bell succeeds **Dr. F. P. Venable** as head of the department of chemistry at the University of North Carolina. While Dr. Venable has resigned as head of the chemistry department, he will continue his duties as professor. In the fall, **Dr. F. C. Vilbrandt** of Ohio State University will assume his duties at the University of North Carolina as associate professor of industrial chemsitry, and will inaugurate laboratory courses in that subject, as well as carry on the lecture work.

Dr. Eugene P. Deatrick resigned as instructor of soil technology, College of Agriculture, Ithaca, N. Y,, to become associate professor of soils, head of department, West Virginia University, Morgantown, W. Va.

Mr. W. H. Ransom, who has been stationed at the old Hickory Powder Plant as executive officer, for the past two years, has accepted a position with the Celluloid Co., Newark, N. J.

Dr. Arthur B. Ray, who has been directing certain investigations relative to carbon products at the Cleveland laboratories of the National Carbon Co., Inc., has been recently transferred to the Union Carbide & Carbon Research Laboratories, Inc., Long Island City, N. Y.

Mr. Alfred T. Shohl, formerly associate professor of chemical hygiene in the School of Hygiene and Public Health, Johns Hopkins University, has recently been appointed associate professor of pediatrics in the newly created department of pediatrics at the Yale Medical School, New Haven, Conn. A large part of the work will consist of research in food and metabolism connected with children.

Mr. Wallace L. Caldwell, for the past nine years director, department of roads and pavements, of the Pittsburgh Testing Laboratory with headquarters at Birmingham, Ala., is at present located at Louisville, Ky., as assistant to the president of the Kentucky Rock Asphalt Co.

Mr. Ralph C. Holder recently resigned as junior chemist in the food research laboratory, Bureau of Chemistry, to accept a position as chemist in charge of the chemical laboratory for the Collis Products Company at St. Paul, Minn.

Mr. Paul M. Stouffer left the laboratory of the Solvay Process Company in Syracuse, N. Y., to take charge of control work for the White Rock Mineral Springs Co., Waukesha, Wis.

Mr. R. H. Hoffman, food and drug commissioner of the State of Texas, for about ten years, now has charge of the laboratory and the Life Extension Service of the Great Southern Life Insurance Co., Houston, Tex.

Mr. J. P. Bonardi, who has been with the Bureau of Mines Experiment Station at Denver for the past five years, recently transferred to Reno, has accepted a position as manager of the assay and chemical department of the Mines and Smelter Supply Co. of Denver, Col.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

Barytes and Barium Products in 1919. G. W. Stose. Separate from Mineral Resources of the United States, 1919, Part II. 13 pp. Issued July 28, 1921. The barytes industry had a prosperous year in 1919. The following tabular statement shows the quantity, value, and average price per ton of crude barytes produced and marketed in the United States, 1880-1919:

CRUDE BARYTES PRODUCED AND MARKETED IN THE UNITED STATES, 1880-1919

	Quantity Short tons	Value	Average price per ton
Annual average for 10 years 1880-1889..	21,110	....	....
Annual average for 10 years 1890-1899..	27,523	....	....
Annual average for 10 years 1900-1909..	58,310	....	....
Annual average for 5 years 1910-19 14....	43,389	....	$3.31
1915	108,547	$381,[illegible]	3.51
1916	221,952	1,011,232	4.56
1917	206,888	1,171,184	5.66
1918	155,368	1,044,905	6.73
1919	189,647	1,555,793	8.20

The total quantity of barium products manufactured and sold in 1919 was considerably greater than in 1918. The quantity of barium chemicals marketed in 1919 was somewhat less than in 1918, but the quantity of lithopone produced and sold was much greater than in 1918.

Magnesite in 1920. C. G. Yale and R. W. Stone. Separate from Mineral Resources of the United States, 1920, Part II. 17 pp. Published July 27, 1921. Reports received from all producers show that 303,767 short tons of crude domestic magnesite, valued at $2,748,150, was produced and sold or treated in 1920, an increase of 94 per cent in quantity and 120 per cent in value over 1919.

BUREAU OF MINES

Nature of Shale Oil Obtained from Shale Oil Assay Retort Used by the Bureau of Mines. M. J. Gavin and L. C. Karrick. Reports of Investigations. Serial No. 2254. 11 pp. Issued June 1921. Experimental work indicates that it is ossible to vary the quantity and quality of the oil obtainable with the assay retort from a given shale by varying the conditions of retorting.

An Unusual Hazard in Reopening Long-flooded Timbered Metal Mines. D. Harrington. Reports of Investigations. Serial No. 2255. 3 pp. Issued June, 1921. There is a well-defined movement towards reopening of long abandoned mines with intent to extract ores of a grade formerly rejected but probably amenable to present-day methods of treatment. Many of these properties have long been under water and their recovery presents, among other problems, that of possible occurrence of explosive gas, methane. Precautions to be observed in such work are described.

Notes on The Oil-Shale Industry with Particular Reference to the Rocky Mountain District. M. J. Gavin, H. H. Hill and W. E. Perdew. Reports of Investigations. Serial No. 2256. Issued June 1921. 36 pp. As yet no process for obtaining oil from oil shale has been used in actual commercial practice in this country. Indications are that the United States cannot continue long to depend on domestic petroleum to supply completely the demand for petroleum products, and that sooner or later our oil shales will have to be used to help supply the deficit. The shale-oil industry cannot hope to supplant the petroleum industry in a large way for many years.

Six-Year Accident Record of Mines of the Anaconda Copper Mining Company in Montana. D. Harrington. Reports of Investigations. Serial No. 2259. 2 pp. Issued June, 1921.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. Reports of Investigations. Serial No. 22621. 28 pp. Issued June, 1921.

Gases Produced in the Use of Carbon Tetrachloride and Foamite Fire Extinguishers in Mines. A. C. Fieldner and S. H. Katz. Reports of Investigations. Serial No. 2262. 6 pp. Issued June, 1921. A summary of results is included giving the important constituents of the atmospheres produced in the use of carbon tetrachloride and foamite extinguishers in the wood fire experiments.

Monthly Statement of Coal-Mine Fatalities in the United States, April, 1921. W. W. Adams. 9 pp. Issued June, 1921. Paper, 5 cents.

DEPARTMENT OF AGRICULTURE

Waterproofing and Mildewproofing of Cotton Duck. H. P. Holman, B. S. Levine and T. D. Jarrell. Farmers' Bulletin 1157. 13 pp. Paper, 5 cents. Reprinted with slight changes, June 1921.

COMMERCE REPORTS—JULY 1921

Conditions in the Belgian **zinc** industry are described. (P. 38.)

An article describing the Chinese **oil** resources in great detail may be obtained from the Far East Division of the Bureau of Foreign and Domestic Commerce. (P. 54.)

The oil-bearing **nuts** of the Guatemalan **palm** tree are sad to contain 65 per cent of oil, in comparison with 42 per cent for African nuts, and the yield of kernels per ton of nuts in Guatemala is about 18 per cent. (P. 56.)

The exportation of **oil** by American companies in Tampico stopped on July 2, 1921. (P. 65.)

Japan has recently completed a contract with a British company whereby her **fuel oil** tanks will be filled to capacity. (P. 84.)

The **copra** trade in the Dutch East Indies is reviewed. (P. 85.)

The government of Ecuador has drawn up a contract with an American company which provides for the exploitation of **oil** deposits in the province of El Oriente for a period of 34 years. (P. 95.)

One of the effects of the coal famine in England has been to fix attention to the possibilities of **liquid fuel.** Possibilities of steam raising by means of oil installations are looked upon as of more immediate concern than anything else. (Pp. 107-9.)

Great interest is shown at Sydney in the manner in which the **phosphates** from Nauru Island are to be divided among manufacturers of fertilizers. (Pp. 116-7.)

Forty carloads of **mineral fertilizer** destined for Soviet Russia were passed through Yamburg from Germany up to the end of April 1921. (P. 120.)

Announcement comes from Moscow of the success of experiments for the production of **paper** from **flax** waste, which has hitherto remained unused. (P. 120.)

The curtailment of the use of electricity for light and power has led to an interesting development in Liverpool in the installation of **oil fuel** apparatus for light and heat by kinema houses and other places of amusement. (P. 123.)

A new plant and buildings, costing $1,250,000, are in the course of erection by the Cape Explosives Works (Ltd.), Somerset West, Cape Province. They plan to supply every kind of **fertilizer** used in the country and expect to be able within a few months to produce fertilizers at the rate of 100,000 tons per annum. (P. 128.)

The stagnation of the **nitrate** market continues to be the principal item of interest in Chile. (P. 143.)

For the greater part of the year a prohibition on import of **synthetic dyes** was maintained in Bombay, India, in the interest of the British manufacturer. Licenses were, however, freely issued for foreign dyes which Great Britain was unable to produce in sufficient quantities. (P. 154.)

The new Italian import duties, effective July 1, 1921, are quoted on **cottonseed oil** and gasoline. (P. 165.)

It is reported that several tons of high-grade **tin ore** have been extracted near Sao Paulo, Brazil. (P. 167.)

Phosphate production in Egypt is reviewed and it is stated that the industry has rapidly advanced since the signing of the armistice until the 1920 exports were double those of 1919. (P. 183.)

The production of **petroleum** in Mexico from 1901 to 1920 was 563,523,752 bbls. of 42 gal. each. The quantity increased yearly from 10,345 bbls. in 1901 to 163,540,000 bbls. in 1920. It was estimated that in January 1921 the supply of oil in the Tampico-Tuxpam fields was 450,000,000 bbls. This would last 2.5 yrs. at the rate of production in 1920. It appears that there is no ground for anxiety about the future oil supply, though there is some difference of opinion on this subject. (P. 230.)

The British **Cast Iron Research** Association has been formed, its object being to conduct scientific and experimental work in connection with the cast iron trade. (P. 234.)

A new French company has been formed with a capital of 100 million francs to market **oil** in France and the French colonies. Of the capital the French syndicate guarantees the subscription of 55 per cent and the Anglo-Persian Oil Company the remaining 45 per cent. (P. 234.)

Statistics are given showing the total production of **petroleum** for Mexico for the years 1901-1920, inclusive; also the figures for production, exportation, and consumption in 1921, up to and including May. (P. 271.)

The future export tendencies of German **coal-tar colors** are described and the following table is included showing the quantity of aniline and coal-tar dyestuffs exported to various countries in 1920 as compared with the quantity exported to these countries in 1913:

Countries of Destination	1913 Tons	1920 Tons	Countries of Destination	1913 Tons	1920 Tons
United States	13,855	338	Sweden	900	893
Great Britain	11,000	9.0	Switzerland	784	164
Austria-Hungary	5,800	741	Spain	[illegible]	447
Czechoslovakia	....	2,335	Brazil	627	....
Italy	4,100	1,257	Mexico	[illegible]	....
China	8,500	....	Canada	443	....
Japan	3,500	....	Turkey	[illegible]	105
India	3,800	....	Portugal	418	
Belgium	2,500	790	Norway	[illegible]	[illegible]
Russia	1,100	....	Denmark	[illegible]	[illegible]
Holland	1,400	1,047	Finland	[illegible]	[illegible]
France	1,400	6.0			

(Pp. 279-80.)

The **petroleum** industry in Soviet Russia in 1920 is reviewed. In 1920 there was produced 10,000,000 lbs. of crude petroleum more than in 1919. (Pp. 284-7.)

The possibilities of the sale of American **drugs** and **medicines** in India warrant a careful study of the market. (P. 289.)

According to an Indian expert, **oil** may soon be discovered in Bihar and Orissa, in the Central Provinces, and in the Peninsula. There are also indications of a fairly well-defined oil belt between Assam and Burma, passing through Chittagong. (P. 289.)

Word comes from England that the North Staffordshire Railway has, in common with many other companies, adopted **oil-burning** for **locomotives.** An interesting feature of the change is that both coal and oil can be used as fuel at the same time on these locomotives. (P. 317.)

Near-Eastern markets for **paints** and **varnishes,** including Palestine, Smyrna, Syria and Turkey, are reviewed. (Pp. 318-20.)

British trade in **chemicals, drugs** and **dyes** is reviewed. (Pp. 330-3.)

The British **palm-kernel** and **edible-oil** industry is described and in comparing the 1920 with the 1913 status it is noted that the United Kingdom and Germany have exchanged positions in the palm-kernel crushing industry. (Pp. 338-42.)

The **vegetable-oil** industry of Belgium is reviewed. The four years of war had a disastrous effect on the industry from which it has not yet recovered. (Pp. 363-5.)

The production of **salt** in the Fukien Province, China, during 1920 amounted to 40,103 tons. (P. 376.)

A market for **aniline dyes** is said to exist in the Chungking District, China. (P. 376.)

Statistics are given showing the production of **minerals** and metals in the United Kingdom during 1918 and 1919. (Pp. 378-9.)

The Havre trade in **oleaginous nuts** is reviewed. (Pp. 384-5.)

Cellulose of a good quality, capable of being used in the manufacture of fine grades of paper and gunpowder, is manufactured in Jugoslavia. (P. 416.)

Trade in **dyestuffs** in Japan has become more active. (P. 452.)

There were exported 13,901,524 metric quintals of **nitrate** from Chilean ports during the first four months of the present year. (P. 471.)

The Secretary of the Scientific and Industrial Nitrate Institute states that at the present rate of production of nitrate it is possible to extract only 700 tons of **iodine** annually in Chile; that in normal times the production may be estimated at double that figure. (P. 471.)

The slump in exchange during 1920 has completely upset all Chinese business in the **dye** trade. (P. 485.)

STATISTICS OF EXPORTS OF THE UNITED STATES—JUNE 1921

Shanghai—(Pp. 1248-9)
Antimony
  Crude
  Oxide
Albumin
Camphor
Tungsten ore

Cuba—(Pp. 1270-1)
Gold, silver and platinum
Iron and steel
Copper and alloys
Paints and varnishes
Chemical products
Oils
Hides and skins

Jamaica—(P. 1294)
Orange oils
Tanning materials
Copra

London—(P. 1785)
Rubber
Tin
Leather, hides
Drugs and chemicals
Gums

France—(P. 1307)
Chemicals
Colors
Copper
Hides and skins

Leghorn—(P. 1330)
Sienna earth
Umber earth

[illegible], Italy (P. 1519)
Olive oil
Sulfur oil
[illegible]
Manna
Oil of lemon
Oil of orange
Dyeing and tanning materials
[illegible] lime
Citric acid
Tartaric acid

[illegible] (P. 1627)
Creosote oil acids
Fertilizers
[illegible]
Manganese oxide and ore
Sulfate of ammonia

Aleppo, Syria—(P. 1616)
Gum tragacanth

Mexico City—(P. 1738)
Jalap root
Ipomea orizabensis
Indigo
Valerian
Copper
Hides and skins
Linaloa oil
Sesame oil
Quicksilver
Silver
Turpentine

Kalamata, Greece—(P. 1791)
Hides and skins
Resin

Curacao, West Indies—(P. 1807)
Copaiba balsam
Chicle
Gasoline

Algeria—(P. 1869)
Essence of geranium
Glue stock
Iron ore

STATISTICS OF EXPORTS OF THE UNITED STATES—JULY 1921

Indo-China—(P. 15)
Gums, gamboge
Plumbago or graphite
Rubber, India, crude
Sticklac

Brazil—(P. 41)
Carnauba wax
Cottonseed
Manganese
Monazite sand
Rubber

Capetown—(P. 74)
Buchu leaves
Lead and copper
Vanadium
Wax

Liverpool—(P. 123)
Tin
Ferromanganese
Palm oil

Vigo, Spain—(P. 147)
Arsenic
Olive oil

Hamkow, China—(P. 495)
Antimony
Cottonseed oil
Sesamum seed
Tallow, vegetable

Birmingham, England (P. 240)
Aluminium
Chemicals and drugs
Acid, citric
Ammonim carbonate
Ammonim muriate
Soda tartrate
Gelatin

[illegible], India—(Pp. 156-8)
Linseed
[illegible]
Rape seed
Bone meal
[illegible]
Drugs
Gums
Oil
Coconut
Rose
Ore, manganese
Seeds
  Castor
  Poppy
  Mustard

Calcutta, India—(P. 253)
Lac
Linseed
Rapeseed
Castor seed

Greece—(P. 343)
Attar of roses
Chrome ore
Magnesite ore
Opium
Rosin
Saffron
Tartrate of lime

Egypt—(P. 201)
Alcohol
Medical preparations
Oils, mineral

London, England—(P. 510)
Rubber
Tin
Drugs and chemicals

Austria—(Pp. 360-1)
Oils, fats
Paints and tanning materials
Gums and resins
Mineral oils, charcoal and slate tar
Chemical products and chemical materials
Acid tartaric
Fusel oil
Mineral wax

Mexico—(Pp. 579-91)
Citrate of lime
Oil of lime
Oil cake
Coconut
Sesame seed
Silver and lead ore
Copper ore
Manganese ore
Silver ore
Zinc ore
Glycerol, crude
Oils, essential
Molybdenum ore
Tungsten ore
Arsenic
Cottonseed oil
Rosin
Rubber
Turpentine
Wax
Bark
Cinchona
Sarsaparilla
Chicle, crude
Nitrate of potash
Quicksilver

Tampico, Mexico—(Pp. 180-1)
Petroleum

BOOK REVIEWS

Metallography, Part II. The Metals and Common Alloys. By Samuel L. Hoyt, E. M., Ph. D. 1st Edition. x + 462 pages. McGraw Hill Book Co., Inc., New York. 1921. Price, $5.00.

To the general reader the subtitle of this book gives little idea of the valuable material contained in it. While the aluminium alloys, the brasses and bronzes, the bearing metals, steels and cast irons are strictly speaking common alloys they are so important both from a scientific and technical point of view they deserve a better adjective to describe them. In his preface the author refers to them as "the more important metals and alloys" which is much more appropriate. This volume describes the constitution and microstructure, the physical and mechanical properties, the heat treatment, effects of impurities, and the uses of (1) pure metals, (2) white metal alloys, (3) light metal alloys, (4) brasses and bronzes, (5) steel and cast iron, and (6) special steels. The introduction into a book on metallography of a discussion of the properties of the individual metals is a welcome and entirely proper addition, and under this heading the author has collected from the most reliable sources, and discussed the data concerning the more important properties of the metals. Naturally copper and iron receive the greatest attention. For the sake of completeness and on account of its importance, data on nickel should have been included, but unfortunately the author gives none and refers to another publication which may be available to a comparative few. The discussion of the properties of the metals is interesting, concise, accurate, and with abundant reference to the original data.

The author has departed from the usual practice of treating the nonferrous alloys. Instead of classifying them as copper, lead, or zinc base alloys he has grouped them under the headings of bearing metals, light metal alloys, and brasses and bronzes. This scheme has advantages in that under these general headings there can be the older classification according to metals. Under the simple bearing metals, the author discusses the equilibrium diagrams and the properties of the binary alloys, lead-tin, lead-antimony, tin-antimony, etc., and then a few of the ternary alloys.

Under the light metal alloys are discussed the alloys of aluminium with copper, zinc, iron, manganese, silicon, alloys which may be cast, forged, or heat treated. Duralumin, on account of its increasing importance in airplane construction and its unusual change of properties brought about by heat treatment and "ageing," receives fuller discussion.

Although the brasses and bronzes are commercially old and important, it is only comparatively recently that they have received adequate scientific attention. The author traces the development of this work from Charpy's first paper in 1896 to the most recent, and discusses comprehensively the equilibrium diagrams of each group, the mechanical and physical properties, microstructure, effect of impurities. One would naturally expect a discussion of the important phenomena of corrosion and season cracking at this point, but the author is probably reserving it for the volume to follow on "Technical Practice."

The author devotes about two-thirds of the volume to steel, cast iron, and special steels. His statement in beginning the discussion of the iron-carbon constitution diagram that the diagram may be regarded as orthodox has a certain grim humor about it when one considers that it is the foundation stone of all the discussion that follows. The diagram is, however, discussed fully, clearly, and with good judgment. In regard to the austenite-pearlite transformation taking place on slow cooling the author uses excellent judgment, and the logic of the phase rule in dismissing the conception held by some that martensite and troostite are intermediate phases in this transmission. Again he shows discrimination in not being misled by propaganda in favor of certain alloying elements in special steels, or as to the harmless effects of certain impurities such as phosphorus and sulfur in ordinary steels. Indeed, one of the features of the book is the good judgment not only as to choice of material but also as to its relative importance. Nickel, chromium, manganese, silicon, tungsten, molybdenum, chrome-nickel, chrome-vanadium, and high speed steels are discussed with abundant reference to the literature. The collection of data in regard to the physical properties, constitution, critical temperatures, microstructure, and uses of all these steels will be welcomed most heartily. In his discussion of the uses of manganese steel, the author makes the statement that manganese steel containing below 1.5 per cent manganese is used in Europe, especially in Germany, evidently forgetting the recent extensive manufacture of rifles in this country. Such omissions are extremely rare, and on the whole the book is excellent, being clear, concise, accurate, and well balanced.

Henry Fay

Rubber, Resins, Paints and Varnishes. By R. S. Morrell, Ph.D., and A. de Waele, A.T.C. xii + 236 pages. D. Van Nostrand Co., New York, 1920. Price, $4.00 net.

This is one of a series of volumes giving a comprehensive survey of the chemical industries, under the editorship of Dr. Samuel Rideal. As is said in the preface, the object of the books is to "give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture."

The volume will be useful to the nontechnical as well as to the chemical reader, as it gives a brief, but withal an eminently satisfactory, review of the subjects in question, the space devoted to each being as follows: Rubber, 35 pages; drying oils, 42; resins and pitches, 31; pigments and paint, 55; linoleum, 15; varnishes, 51.

Stress is laid upon the chemistry involved—in the case of synthetic rubber, for example—and the action of driers in paints is carefully explained.

Statistics are not included, nor are analytical data or methods, except briefly in the case of varnishes.

It would have been instructive in connection with paints to have given the results of the extensive and practical tests on paint made in the United States by Holley and Ladd and Gardner, and by the American Society for Testing Materials.

A well-selected bibliograph with each chapter is a useful feature.

The book may be recommended cheerfully to all who have occasion to deal with the subjects in question as an interesting and authoritative treatise on their occurrence, the chemistry of their manufacture, and their uses.

A. H. Gill.

American Chemistry. By Harrison Hale. vii + 215 pages. D. Van Nostrand Co., New York, 1921. Price. $2.00.

Here is a little book with a most attractive title, written with an excellent purpose: "It seeks to be of service both to the general reader and to the reader still in school. For the student, it is intended for use either as collateral reading along with a course in General Chemistry, or as a short separate course."

Essentially then, this is to be a popular instructive treatment of a great subject. It is eminently true that the treatment of a subject such as chemistry in simple language, suited to the layman, requires greater care than its presentation to those conversant with the rudiments of the science. In the former case, statements must either be entirely comprehensible to one with a good general education, or must convey the impression to such a reader that the meaning is clear to him. He must encounter few words with which he is not familiar, even though he may not be aware of their full meaning. Too many unknown words soon cause him to lose interest, and to feel that the subject is beyond his understanding. It must be said that, unfortunately, in this book, the author has failed to meet this requirement. For example, how can the unprepared reader gain any pleasure from statements such as these:

> More recently by treating cottonseed oil with hydrogen in the presence of a catalyzer, the melting point is raised due to an increase in the molecular weight of certain constituents, and so a larger amount of solid fat can be obtained.
>
> At higher temperatures the heavy oils with the heavier molecule tend to break up into oils with a lower boiling point and smaller molecular weight. This process is called "cracking."
>
> Hence all drying oils are chemically unsaturated compounds, that is all of their valency bonds are not satisfied, and these bonds are filled by the oxygen upon exposure to the air.

The book contains chapters on a number of subjects of very live interest, subjects which should be brought to the attention of the public from a chemist's point of view, but these are handled here in a haphazard, careless fashion which does not give any proper sequence to the facts, or make them stand out in their true relation to each other. The book reads, in fact, as though it were a collection of verbatim notes taken at lectures given by one who had prepared only by reading a number of descriptive articles such as those quoted as references.

It must be said that this carelessness goes even beyond the mere construction of the chapters. It is to be found in the English used and in the inaccuracy of the proofreading. Those who write as members of the class of educators, should be careful to use pure, clear English. Here we read:

> The advantages of the American system, now in very general use in this country, are lower construction cost, greatly lessened requirement of land for the buildings and the ease of washing the filter, which is generally carried out daily by the use of compressed air followed by filtered wash water forced up from below and allowed to run to waste.
>
> In addition to this, certain substances, not all of which are clearly understood, are necessary to control and regulate body processes.
>
> The increased use of paint materials has without doubt made, not only for improved sanitary conditions and more beautiful surroundings, but also for economy on account of the protection from rot and rust resulting from the action of the atmosphere and of moisture.

In addition, the pit-falls of "as to" and of split infinitives are not avoided.

It would be foolish to take space in such a Journal to point out short-comings of this kind, were it not that they are characteristic of a great deal of the simplified science writings of today. Would it be too much to ask of those about to publish matters of this kind to have someone accustomed to criticize English pass upon their manuscript? There are some surprising statements in consequence of careless wording in this little book. We read that nitrogen is used (!) as "a diluent for the more active oxygen of the air," and again, that "one of the uses (!) of nitrogen in the air is to dilute the more active oxygen." Presumably, this should have been mentioned in the first chapter of Genesis. Again, cellulose is "named from the plant cells of which it is made," and finally, the North American Indians in 1659 sold crude oil as an "external and internal medicine, frequently being sold as Seneca oil."

It is a pity that this book is not better. Its faults overshadow its virtues, chief among which is that of listing numerous references which are likely to prove of interest and benefit to students beginning their study of chemistry.

R. E. Rose

Copper Refining. By Lawrence Addicks, Consulting Engineer. ix + 211 pp. McGraw-Hill Book Co., Inc., New York, 1921. Price, $3.00.

The volume is a timely and valuable addition to a library on the metallurgy of copper. As the title indicates, the text is strictly limited to the purification of blister copper. The thirteen chapters discuss the following general subjects: metal losses, metals in process, tank resistance, current density, current efficiency, impurities, by-products, furnace refining, the requirements of refined copper, copper from secondary material, the power problem, elements of design, and applications to other fields. The discussions under the general headings are well designed, the subdivisions being clearly stated and well developed in order. This is one of the many strong points in the book and helps to make it thoroughly readable and easily grasped. The flow sheets of a copper refining plant, and those dealing with the different phases of the refining process are admirably worked out in clear detail and add greatly to the descriptive matter which they accompany. The whole work appears to be well up-to-date and offers many suggestions for investigation of new processes for improved efficiency and for the prevention of waste. Very little theory is developed in the book, though the results of modern theories are used wherever applicable. One may summarize the text by saying that it is a clear description of modern copper refining practice together with the application of the principles upon which the practice is based.

As is common in first imprints of a book there are a number of typographical errors, some rather glaring, and occasionally there is a poor English sentence. Only one serious error was noticed in applying principles. This is in the discussion of the order of oxidation of the metals based upon the heats of formation of the oxides. The author makes his comparison with molar heats, rather than with equivalents, and thus wrongly concludes that tin would be oxidized to the dioxide in preference to zinc. From the thermochemical data given, however, zinc would reduce stannic oxide with the evolution of heat, and thus would become oxidized in preference to tin.

Since both the series and multiple arrangements of the electrodes in the tanks are in commercial use, the reviewer would have welcomed a discussion of the relative efficiencies of the two types of connection under varying conditions. On the whole, the text rather exceeds one's expectations regarding a subject on which so little had been compiled.

J. H. Ransom

NEW PUBLICATIONS

Flotation: Concentration by Flotation. Compiled and edited by T. A. RICKARD. 692 pp., Illustrated. Price, $7.00 postpaid. John Wiley & Sons, Inc., New York.

Metallurgy of the Common Metals. LEONARD S. AUSTIN. 5th edition, revised and enlarged. 615 pp. Illustrated. Price, $7.00. John Wiley & Sons, Inc., New York.

RECENT JOURNAL ARTICLES

Aluminum: Losses in Aluminum and Aluminum Alloy Melting. ROBERT J. ANDERSON. BRASS WORLD, Vol. 17 (1921), No. 6, pp. 154-56.

Aluminum: Metodo Gasvolumetrico per la Determinazione dell' Alluminio. L. LOSANA. GIORNALE DI CHIMICA INDUSTRIALE ED APPLICATA, Vol. 3 (1921), No. 6, pp. 239-41.

Catalysis: Le Mecanisme de l'Action Catalytique. CH. MATIGNON. CHIMIE ET INDUSTRIE, Vol. 6 (1921), No. 1, pp. 7-10.

Cement: Relation between Tensile and Compressive Strengths of Cement Mortars. J. R. DWYER. CONCRETE, Vol. 18 (1921), No. 6, pp. 123-25.

Cement: The Relation of Carbon Dioxide and Moisture to the Setting Time of Cement. S. L. MEYERS. CONCRETE, Vol. 19 (1921), No. 1, pp. 128-30.

Coal: The Use of Oil in Cleaning Coal. G. ST. J. PERROTT and S. P. KINNEY. COAL AGE, Vol. 20 (1921), No. 4, pp. 132-134; CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 5, pp. 182-88.

Coal: The Scope of Pulverized Coal. F. P. COFFIN. COMBUSTION. Vol. 5 (1921), No. 2, pp. 62-65, 82.

Coal: Les Matières Volatile de la Houille. ACHILLE DELCLÈVE. CHIMIE ET INDUSTRIE, Vol. 6 (1921), No. 1, pp. 33-40.

Coal: Some of the Many Problems in the Cleaning of Coal. EDWARD O'TOOLE. COAL AGE, Vol. 20 (1921), No. 1, pp. 3-6.

Colloids: In Relation to Clarification in Sugar Manufacture. STUART M. LITTLEMORE. CHEMICAL ENNGINEERING AND MINING REVIEW, Vol. 13 (1921), No. 153, pp. 319-22.

Copper: Principles of Leaching and Precipitation of Copper. FRANK A. LATHE. CANADIAN CHEMISTRY AND METALLURGY, Vol. 5 (1921), No. 7, pp. 202, 203.

Corrosion: Les Corrosion du Fer et leur Suppression par le Degazage de l'Eau. G. PARIS. CHIMIE ET INDUSTRIE, Vol. 6 (1921), No. 1, pp. 11-32.

Cottonseed: Chemical Changes in Cottonseed during Heat and Storage. JOHN MALOWAN. THE COTTON OIL PRESS, Vol. 5 (1921), No. 4, pp. 40-43.

Dyeing: A Study of the Variations in Hematine Dyeings with Different Methods of Chrome Mordanting. CARL W. STAPLES. TEXTILE COLORIST, Vol. 43 (1921), No. 511, pp. 463-466; No. 512, pp. 528-31.

Dyeing: Dyestuff Testing in the Textile Industry. EDW. WALLACE PIERCE. CANADIAN DYER AND COLOR USER, Vol. 1 (1921), No. 7, pp. 132-36.

Dyeing: The Mechanical Ventilation of Dyehouses. J. E. BRIERLEY. JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS, Vol. 37 (1921), No. 7, pp. 187-90.

Explosion Hazard and its Prevention. JOSEPH F. SHADGEN.. THE IRON AGE, Vol. 108 (1921), No. 3, pp. 127-30; No. 4, pp. 205-06, 289-40.

Gasoline: Problems of Motor Gasoline. E. W. DEAN. PETROLEUM, Vol. 11 (1921), No. 4, pp. 40, 45.

Gelatin: Les Propriétés de la Gélatine. L. MEUNIER. CHIMIE ET INDSTRIE, Vol. 5 (1921), No. 6, pp. 642-50.

Glass. The Manufacture of Constructional Glass in the United States. E. WARD TILLOTSON, JR. JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY, Vol. 40 (1921), No. 13, pp. 155t-59t.

Heat Losses: Minimizing Steam Boiler Losses. ROBERT JUNE. THE GAS AGE, Vol. 48 (1921), No. 1, pp. 7-9.

Heat Waste: Stopping Wastes in the Boiler Plant. LOREN L. HEBBERD. SUGAR, Vol. 23 (1921), No. 7, pp. 384-86.

Industrial Safety: The Engineer's Part in Industrial Safety. C. P. TOLMAN. CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 5, pp. 203-05.

Iron: Electric Reduction of Iron Ores. H. A. de FRIES. CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 5, pp. 193-94.

Lead: Notes on the So-called Action of Water on Lead. JOHN C. THRESH. THE ANALYST Vol. 46 (1921), No. 544, pp. 270-79.

Leather: Further Observations on the Wilson-Kern Method of Tannin Analysis. G. W. SCHULTZ. JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION, Vol. 16 (1921), No. 7, pp. 349-67.

Lime: The Dependence of the Lime Industry upon Nature and Science. ARTHUR D. LITTLE. CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 4, pp. 149-52.

Metallization: Les Progrès de la Metallisation: Procédé Schoop par Pulvérisation de Metaux ou Alliages Fondus. P. NICOLARDOT. CHIMIE ET INDUSTRIE, Vol. 5 (1921), No. 6, pp. 619-35.

Nitrous Gases: The Effect of the Presence of Chlorine on the Absorption of Nitrous Gases. H. W. WEBB. JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY, Vol. 40 (1921), No. 13, pp. 162t-65t.

Palm Oil: Un Nouvel Emploi de l'Huile de Palme. I. LAZENNEC. L'INDUSTRIE CHIMIQUE, Vol. 8 (1921), No. 90, p. 262.

Petroleum: The Colloid Chemistry of Petroleum. FRED. W. PADGETT. CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 5, pp. 189-92.

Phosgene: Azione del Fosgene sulla Ricinoleina. ARNOLDO PIUTTI and A. CURZIO. GIORNALE DI CHIMICA INDUSTRIALE ED APPLICATA, Vol. 3 (1921), No. 6, pp. 242-44.

Pulp: Dyeing of Straw Pulp. CLARENCE J. WEST. PAPER, Vol. 28 (1921), No. 16, pp. 23-24.

Rubber: Experimental Vulcanization on the Small Scale. D. F. TWISS and S. A. BRAZIER. THE INDIA-RUBBER JOURNAL, Vol. 62 (1921), No. 1, pp. 15-17.

Rubber: Pitch Hydrocarbons used in the Rubber Industry. FREDERIC DANNERTH. THE INDIA RUBBER WORLD, Vol. 64 (1921), No. 5, pp. 821-24.

Steel: An Occurrence of Nitrogen in Steel. A. A. BLUE. THE IRON

Rubber: The Presence of Manganese in Raw Rubber and the Origin of Tackiness. G. BRUNNI and C. PELIZZOLA. THE INDIA-RUBBER JOURNAL, Vol. 62 (1921), No. 3, pp. 13-14.

Rubber: Vulcanization of Rubber in Sol and Gel Forms. HENRY P. STEVENS. THE RUBBER AGE, Vol. 9 (1921), No. 8, pp. 295, 297.

Starch: The Manufacture of Starch, Glucose and By-Products. R. H. WILLIAMS. CANADIAN CHEMISTRY AND METALLURGY, Vol. 5 (1921), No. 7, pp. 195-96.

AGE Vol. 108 (1921), No. 1, pp. 1-5.

Sugar: Making Crystalline Dextrose. CHR. E. G. PORST. SUGAR, Vol. 23 (1921), No. 7, pp. 380, 381.

R. G. TILLERY. LOUISIANA PLANTER AND SUGAR MANUFACTURER, Vol. 66 (1921), No. 26, pp. 411-14.

Sugar: Preliminary Studies on some Fungi and Bacteria Responsible for the Deterioration of South African Sugars. PAUL A. VAN DER BIJL. INTERNATIONAL SUGAR JOURNAL, Vol. 23 (1921), No. 270, pp. 320-24.

Sugar: On Refining Raw Sugars Commercially Using Vegetable Carbons.

Sugar: The Use of Vegetable Decolorizing Carbons. P. SMIT. THE LOUISIANA PLANTER AND SUGAR MANUFACTURER. Vol. 67 (1921), No. 5, pp. 76-79.

Sugar: Water Concentration: A Neglected Factor in Polariscopic Methods of Sugar Analysis. C. A. BROWNE. LOUISIANA PLANTER AND SUGAR MANUFACTURER, Vol. 67 (1921), No 3, pp. 44-46.

Sulfite Liquor: L'Utilization des Lessives Residuaires de Fabrication des Celluloses à Papier. H. BRAIDY. REVUE GÉNERALE DES MATIÈRES COLORANTES DE LA TEINTURE, DE L'IMPRESSION ET DES APPRÊTS, Vol. 25 (1921), No. 923, pp. 65-70.

Textiles: Faults in Fabrics Due to Chemical Causes. D. K. COLLEDGE. AMERICAN DYESTUFF REPORTER, Vol. 9 (1921), No. 1, pp. 18-20.

Textiles: Notes on some Recent Improvements in the Finish of Linen and Cotton Goods. M FORT. JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS, Vol. 37 (1921), No. 6, pp. 161-66.

Textiles: The Uses of Copper Salts in Textile Treatment. A. J. HALL. AMERICAN DYESTUFF REPORTER, Vol. 9 (1921), No. 5, pp. 21, 24; No. 5, pp. 20, 25, 26. From DYER AND CALICO PRINTER.

The University and Research. VERNON KELLOGG. SCIENCE, Vol. 54 (1921), No. 1384, pp. 19-23.

Varnish: Progrés Réalisés dans la Fabrication des Vernis à la Colophane. CH. COFFIGNIER. CHIMIE ET INDUSTRIE Vol. 5 (1921), No. 5, pp. 495-99.

Vitamines in Food Substances. THE CHEMICAL AGE (London), Vol. 4 (1921), No. 105, pp. 690-92.

Vitamines: Methods of Extracting and Concentrating Vitamines A, B, and C, together with an Apparatus for Reducing Milk, Fruit Juices, and Other Fluids to a Powder without Destruction of Vitamines. J. F. McCLENDON. JOURNAL OF BIOLOGICAL CHEMISTRY Vol. 47 (1921), No. 2 pp. 411-20.

Waste: Disposal of Industrial Wastes and Stream Pollution. .C. A. EMERSON, JR. JOURNAL OF THE FRANKLIN INSTITUTE, Vol. 191 (1921), No. 6, pp. 807-18.

MARKET REPORT—AUGUST, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	August 1	August 15
Acid, Boric, cryst., bbls........lb.	.13¼	.12¾
Hydrochloric, com'l, 20°...lb.	.01½	.01½
Hydriodic ....oz.	.19	.19
Nitric, 42°..................lb.	.07¼	.07¼
Phosphoric, 50% tech.......lb.	.13	.12
Sulfuric, C. P...............lb.	.07	.07
Chamber, 66°..........ton	18.00	18.00
Oleum 20%............ton	22.00	22.00
Alum, ammonia, lump..........lb.	.03½	.03½
Aluminium Sulfate (iron-free)..lb.	.03	.03
Ammonium Carbonate, pwd.....lb.	*.07	*.07
Ammonium Chloride, gran......lb.	*.06¾	*.06¾
Ammonia Water, carboys, 26°..lb.	.08	.08
Arsenic, white..................lb.	.06½	.06½
Barium, Chloride..............ton	*5[illegible].50	*52.00
Nitrate ....lb.	.08¼	*.08¼
Barytes, white.................ton	30.00	30.00
Bleaching Pwd.,35%, works, 100 lbs.	2.25	2.25
Borax, cryst., bbls.............lb.	.06	.05¾
Bromine, pure..................lb.	.27	.27
Calcium Chloride, fused........ton	28.75	28.75
Chalk, precipitated, light.......lb.	.04	.04
China, Clay, imported..........ton	18.00	18.00
Copper Sulfate.............100 lbs.	5.62½	5.62½
Feldspar ....ton	8.00	8.00
Fuller's Earth.............100 lbs.	1.00	1.00
Iodine, resublimed.............lb.	3.50	3.50
Lead Acetate, white crystals....lb.	.13	.12
Nitrate ....lb.	.15	.15
Red American.........100 lbs.	.11¼	.11½
White American........100 lbs.	.09½	.09½
Lime Acetate.............100 lbs.	2.00	2.00
Lithium Carbonate.............lb.	*1.40	*1.40
Magnesium Carbonate, tech.....lb.	.10	.10
Magnesite ....ton	72.00	72.00
Mercury flask...............75 lbs.	*46.00	*45.00
Phosphorus, yellow.............lb.	.30	.30
Plaster of Paris............100 lbs.	1.50	1.50
Potassium Bichromate..........lb.	.11½	.11½
Bromide, imported..........lb.	*.18	*.18
Carbonate, calc., 80-85%....lb.	.05	.05
Chlorate, cryst.............lb.	*.08	*.08
Hydroxide, 88-92%..........lb.	.04¾	.04½
Iodide, bulk................lb.	2.75	*2.65
Nitrate ....lb.	.10	.10
Permanganate, U. S. P....lb.	*.27	*.25
Salt Cake, bulk................ton	25.00	25.00
Silver Nitrate..................oz.	.41½	.42
Soapstone, in bags.............ton	12.00	12.00
Soda Ash, 58%, bags......100 lbs.	2.10	2.10
Caustic, 76%..........100 lbs.	3.80	3.80
Sodium Acetate.................lb.	.06	.06
Bicarbonate ....100 lbs.	2.25	2.25
Bichromate ....lb.	.08	.08
Chlorate ....lb.	.07½	.07½
Cyanide ....lb.	.20	.20
Fluoride, technical..........lb.	*.10½	*.10
Hyposulfite, bbls........100 lbs.	3.50	3.50
Nitrate, 95%...........100 lbs.	2.20	2.20
Silicate, 40°................lb.	.01½	.01½
Sulfide ....lb.	.06	.06
Bisulfite, powdered..........lb.	.06	.06
Strontium Nitrate..............lb.	.12	.12
Sulfur, flowers............100 lbs.	3.00	3.00
Crude ....long ton	20.00	20.00
Talc, American, white..........ton	18.00	18.00
Tin Bichloride..................lb.	.18	.18
Oxide ....lb.	.40	.40
Zinc Chloride, U. S. P..........lb.	.35	.35
Oxide, bbls.................lb.	.09	.09

ORGANIC CHEMICALS

	August 1	August 15
Acetanilide ....lb.	*.27	*.28
Acid, Acetic, 28 p. c........100 lbs.	2.50	2.50
Glacial ....lb.	.10	.10
Acetylsalicylic ....lb.	*.60	*.60
Benzoic, U.S.P., ex-toluene..lb.	.65	.65
Carbolic, cryst., U.S.P., drs..lb.	10	.10
50- to 110-lb. tins.......lb.	.21	.21
Citric, crystals, bbls........lb.	*.45	*.45
Acid (Concluded)		
Oxalic, cryst., bbls..........lb.	.17	.16½
Pyrogallic, resublimed.......lb.	1.75	1.75
Salicylic, bulk, U. S. P......lb.	*.20	*.19
Tartaric, crystals, U. S. P...lb.	*.28	*.27
Trichloroacetic, U. S. P.....lb.	4.40	4.40
Acetone, drums...................lb.	.12½	.12½
Alcohol, denatured, complete...gal.	.37	.35
Ethyl, 190 proof...........gal.	4.75	4.75
Amyl Acetate....................gal.	2.15	2.15
Camphor, Jap, refined..........lb.	.77	.72
Carbon Bisulfide................lb.	.06	.06
Tetrachloride ....lb.	.10½	.10½
Chloroform, U. S. P............lb.	.38	.38
Creosote, U. S. P...............lb.	.40	.40
Cresol, U. S. P..................lb.	.17	.17
Dextrin, corn..............100 lbs.	2.85	2.85
Imported Potato...........lb.	.07	.07
Ether, U. S. P., conc., 100 lbs...lb.	.16	.16
Formaldehyde ....lb.	.13	*.12½
Glycerol, dynamite, drums......lb.	.12½	.13
Methanol, pure, bbls...........gal.	1.25	1.25
Pyridine ....gal.	2.75	2.75
Starch, corn..............100 lbs.	2.28	2.28
Potato, Jap................lb.	.05	.05
Rice ....lb.	.18	.18
Sago ....lb.	.04½	.04½

OILS, WAXES, ETC.

	August 1	August 15
Beeswax, pure, white...........lb.	.40	.37
Black Mineral Oil, 29 gravity..gal.	.22	.22
Castor Oil, No. 3..............lb.	.08½	.09
Ceresin, yellow.................lb.	.10	.08½
Corn Oil, crude, tanks, mills....lb.	.06¼	.06¾
Cottonseed Oil, crude, f.o.b. mill.lb.	.06¾	.07
Linseed Oil, raw (car lots)....gal.	.78	.73
Menhaden Oil, crude (south'n).gal.	.30	.30
Neat's-foot Oil, 20°..........gal.	1.00	1.00
Paraffin, 128-130 m. p., ref......lb.	.06	.06
Paraffin Oil, high viscosity....gal.	.15	.15
Rosin, "F" Grade, 280 lbs......bbl.	5.40	5.40
Rosin Oil, first run............gal.	.35	.35
Shellac, T. N...................lb.	.52	.44
Spermaceti, cake................lb.	.30	.30
Sperm Oil, bleached winter,38°.gal.	1.73	1.73
Stearic Acid, double-pressed....lb.	.09½	.09
Tallow, Oil, acidless............gal.	.65	.65
Tar Oil, distilled..............gal.	.60	.60
Turpentine, spirits of..........gal.	.59	.65

METALS

	August 1	August 15
Aluminium, No. 1, ingots........lb.	.21	.21
Antimony, ordinary........100 lbs.	4.87½	4.87½
Bismuth ....lb.	1.50	1.50
Copper, electrolytic............lb.	.12	.11¾
Lake ....lb.	.12¼	.12
Lead, N. Y......................lb.	.04½	.04½
Nickel, electrolytic.............lb.	.41	.41
Platinum, refined, soft..........oz.	72.00	72.00
Quicksilver, flask.........75 lbs. ea.	46.00	45.00
Silver, foreign..................oz.	.61	.61⅞
Tin ....lb.	.27	.27
Tungsten Wolframite......per unit	3.25	3.25
Zinc, N. Y.................100 lbs.	4.50	4.50

FERTILIZER MATERIALS

	August 1	August 15
Ammonium Sulfate, export.100 lbs.	2.15	2.15
Blood, dried, f. o. b. N. Y......unit	3.00	3.00
Bone, 3 and 50, ground, raw...ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia	4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works ....unit	2.90 & .10	2.90 & .10
Phosphate Rock, f. o. b. mine:		
Florida Pebble, 68%.........ton	5.00	5.00
Tennessee, 78-80%..........ton	8.00	8.00
Potassium Muriate, 80%.......unit	.90	.90
Pyrites, furnace size, imp'ted..unit	.14	.14
Tankage, high-grade, f. o. b. Chicago ....unit	2.25 & .10	2.25 & .10

* Resale or Imported (not an American Maker's price).

COAL-TAR CHEMICALS

Crudes		August 1	August 15
Anthracene, 80-85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U. S. P.	lb.	.18	.17
Cresylic Acid, 97-99%	gal.	.90	.80
Naphthalene, flake	lb.	.07	.07
Phenol, drums	lb.	.10	.10
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.60	.45

Intermediates

		August 1	August 15
Acids:			
Anthranilic	lb.	1.50	1.50
Benzoic, tech.	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.30	1.30
Gamma	lb.	3.00	3.00
H.	lb.	1.15	1.15
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.75	2.75
Naphthionic, crude	lb.	.70	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.29	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.18	.18
For Red	lb.	.42	.42
Aniline Salt	lb.	.26	.26
Anthraquinone	lb.	1.75	1.75
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech.	lb.	.50	.50
U. S. P.	lb.	1.50	1.50
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	5.00	5.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.45	.45
Dinitrobenzene	lb.	.25	.25
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.65
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.50	1.50
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.00	2.00
a-Naphthylamine	lb.	.38	.38
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist.	lb.	.32	.32
m-Nitroaniline	lb.	.95	.95
p-Nitroaniline	lb.	.80	.80
Nitrobenzene, crude	lb.	.12	.12
Rectified (Oil Mirbane)	lb.	.13½	.13½
p-Nitrophenol	lb.	.75	.65
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.85	.85
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.50	1.50
Phthalic Anhydride	lb.	.40	.40
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.65	.60
Resorcinol, tech.	lb.	1.50	1.50
U. S. P.	lb.	1.75	1.75
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.42	.42
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.45	.45
o-Toluidine	lb.	.25	.25
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors		August 1	August 15
Black	lb.	.80	.80

Acid Colors (Concluded)		August 1	August 15
Blue	lb.	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III.	lb.	.50	.50
Red	lb.	1.00	1.00
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Brythrosin	lb.	7.50	7.50
Indigotin, conc.	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.70	.70

Direct Colors		August 1	August 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc.	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors		August 1	August 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors		August 1	August 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors		August 1	August 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.75	.75
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors		August 1	August 15
Auramine, O, domestic	lb.	2.25	2.25
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	2.00	2.00
Methylene Blue, tech.	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol.	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc.	lb.	10.00	10.00
Victoria Blue, base, domestic	lb.	5.40	5.40
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of

INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society

Editor: CHAS. H. HERTY

Assistant Editor: LOIS W. WOODFORD

Advisory Board: H. E. BARNARD, J. W. BECKMAN, A. D. LITTLE, A. V. H. MORY, CHAS. L. REESE, GEO. D. ROSENGARTEN, T. B. WAGNER

EDITORIAL OFFICES:
One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613-0614

Cable Address: JIECHEM

ADVERTISING DEPARTMENT:
170 Metropolitan Tower
New York City
TELEPHONE: Gramercy 2145

Volume 13 OCTOBER 1, 1921 No. 10

CONTENTS

AMERICAN VISIT, SOCIETY OF CHEMICAL INDUSTRY 862

ANNUAL MEETING, AMERICAN CHEMICAL SOCIETY:

- From the Tower 865
- Council Meeting 865
- Story of the Week 866
- Address of Welcome. John E. Teeple 866
- Chemistry and the State. Francis P. Garvan 866
- Modern Developments in War Making. Sir William J. Pope 874
- A Plan for the Development of Industrial Research in Canada. R. F. Ruttan 876
- International Meeting 881
- Side Lights 885

SEVENTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES 886

ORIGINAL PAPERS:

- Camphor Substitutes in the Manufacture of Celluloid. Albert Parsons Sachs and Oscar Byron 893
- The Catalytic Oxidation of Petroleum Oils. C. E. Waters 901
- The Action of Anhydrous Stannic Chloride on Petroleum and Its Distillates. Gregory Torossian 903
- Production of Coumarins from Maleic and Malic Acids. G. C. Bailey and F. Boettner 905
- Condensation Temperatures of Gasoline- and Kerosene-Air Mixtures. Robert E. Wilson and D. P. Barnard, 4th 906
- The Total Sensible Heats of Motor Fuels and Their Mixtures with Air. Robert E. Wilson and D. P. Barnard, 4th 912
- Studies of Wheat Flour Grades. II. Buffer Action of Water Extracts. C. H. Bailey and Anna C. Peterson 916
- Grape-Seed Oil. Frank Rabak 919
- The Effect of Some Decolorizing Carbons upon the Color and Colloids of Cane Juice. Joseph F. Brewster and William G. Raines, Jr. 921
- Dry Substance in Molasses, Sirups and Juices by the Spencer Electric Oven. George P. Meade 924
- The Determination of Reducing Sugars in Lead-Preserved Cane Juices. Joseph B. Harris 925
- The Preservation of Fish Frozen in Chilled Brine. I—The Penetration of Salt. L. H. Almy and E. Field 927
- Measuring Soil Toxicity, Acidity, and Basicity. R. H. Carr 931
- Studies of the Availability of Organic Nitrogenous Compounds—Part I. C. S. Robinson, O. B. Winter and E. J. Miller 933
- The Chemical Constitution of Soda and Sulfate Pulps from Coniferous Woods and Their Bleaching Qualities. Sidney D. Wells 936
- The Determination of Vanadium and Chromium in Ferrovanadium by Electrometric Titration. G. L. Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright 939
- Effect of Variation in Analytical Constants of Linseed and Soy-Bean Oils upon the Quantitative Determination of Linseed Oil in Mixtures of the Two Oils by Means of the Iodine and Hexabromide Numbers of the Fatty Acids. Edward A. Tschudy 941
- Preparation of Alcoholic Potassium Hydroxide Volumetric Solution. S. T. McCallum 943

LABORATORY AND PLANT:

- Need of a New Table for Specific Gravity and Per cent of Glycerol. L. W. Bosart 944
- The Sewage Testing Station of the Illinois State Water Survey Division. Edward Bartow 945

ADDRESSES AND CONTRIBUTED ARTICLES:

- Dyes Derived from Beta-Oxynaphthoic Acid and from J-acid, with Reference to the Chemical Foundation Patents. A. Willard Joyce 946
- Definition of Limits for Impurities in Chemicals—Sulfate in Nitric Acid. W. D. Collins 948

SOCIAL INDUSTRIAL RELATIONS:

- Social Research. H. W. Jordan 949

SCIENTIFIC SOCIETIES:

- Sixty-second Meeting, American Chemical Society, New York, N. Y., September 6 to 10, 1921; The Effect of Chemical Reagents in the Microstructure of Wood—Correction; The Electric Production of Sodium and Potassium Permanganates from Ferromanganese—Correction; Calendar of Meetings 951

MISCELLANEOUS:

- The Société de Chimie Industrielle 904
- Association of Official Agricultural Chemists 943
- Technical Association of the Pulp and Paper Industry 943

WASHINGTON LETTER 961
PARIS LETTER 962
INDUSTRIAL NOTES 963
PERSONAL NOTES 963
GOVERNMENT PUBLICATIONS 964
BOOK REVIEWS 967
NEW PUBLICATIONS 970
MARKET REPORT 971

Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted.
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.
Member of Audit Bureau of Circulations

AMERICAN VISIT, SOCIETY OF CHEMICAL INDUSTRY

Montreal Meeting

Smooth seas and bright skies brought to Canada in happy mood, the delegation of British members of the Society of Chemical Industry, several days in advance of the date set for the Annual Meeting, which was to be held in Canada for the first time in the history of the Society. During this intervening period the visitors were given their first insight into the generous hospitality in store for them, and the time passed pleasantly with informal entertainment and days upon the golf courses.

On Monday, August 29, matters were astir in the chemistry building of McGill University and at 11 A. M. the large lecture room was filled to overflowing. It needed no student of psychology to detect the keen air of interest which reflected the consciousness on the part of all that in this room were assembled representatives of leaders in chemistry in the Anglo-Saxon world, for besides British and Canadians many Americans were present, including four past presidents of the American Chemical Society, all sympathetically agreed upon a conference which should prove not only intellectually stimulating but which should mark the beginning of an era of good will and mutual understanding of deepest import in modern chemical developments.

At this initial meeting Sir William Pope presided as retiring president of the Society of Chemical Industry. Following the usual precedent, his term of office expired during the meeting, but with the customary grace of the Canadians, the newly elected president, Dr. R. F. Ruttan of McGill University, Montreal, insisted that the past president continue to act in an official capacity throughout the meetings in Canada and America. This little instance is indicative of the fine feeling which existed throughout the three weeks which marked the official visit of the British chemists. At the outset of the formal meeting a hearty welcome to the Province of Quebec was given by Sir Charles Fitzpatrick, Lieutenant-Governor of the Province. His words were simple and sincere, but filled with an inimitable wit which at once gave an atmosphere of cheeriness and good will. Professor Watson Bain of the University of Toronto, president of the Canadian Institute of Chemistry, spoke next. Professor Bain's sterling accomplishments in university efforts to promote industrial chemistry and his success in coöperation with the efficient work of the secretary of the Institute, Mr. Harold J. Roast, gave added dignity and weight to the cordial words of welcome which he expressed.

In reply to these addresses Sir William Pope spoke in behalf of the visitors. The applause which greeted his introduction was a fitting tribute from those present to one who had done so much in the field of pure science, who then had thrown himself so whole-heartedly to applying chemistry to war problems for his country, and who following the war had shown such masterly leadership as president of an organization which deals primarily with the applications of chemistry. He typified a life of well-rounded development and broad sympathies, and his achievements which gave him so high a place in public esteem were added to by the ability which he displayed immediately, speaking so directly and with such graceful diction in response to the generous words of welcome previously extended.

Council Report

The report of the Council brought out a number of interesting matters. To those of us who had been so troubled about the increase in dues in the American Chemical Society, it was interesting to note that the Society of Chemical Industry had not hesitated twice on recent occasions to increase the dues. The result has been a year of activities unprecedented in the history of the Society and a small unexpended balance of income shown on the treasurer's books.

Another important development shown by the reports of the Council is the evident closer contact which is being formed between the Society and the Chemical Society of London, especially as to publications. More and more is it being realized that such coöperation will be of the greatest mutual benefit, and these points of contact are no longer theoretically being discussed, but are actually being developed.

In further evidence of the fine financial status of the Society was a report concerning the bequest by Dr. Rudolph Messel. One-fifth of his estate was bequeathed to the Society subject to certain annuities. The executors have now turned over to the Society the sum of £17,000 and in a short while this amount is to be increased by further additions from the estate amounting to £1339. Plans for the best method for expenditure of the interest on this bequest are now being formulated. It has already been determined to hold an annual Messel lecture and to confer a medal to be named in honor of Dr. Rudolph Messel.

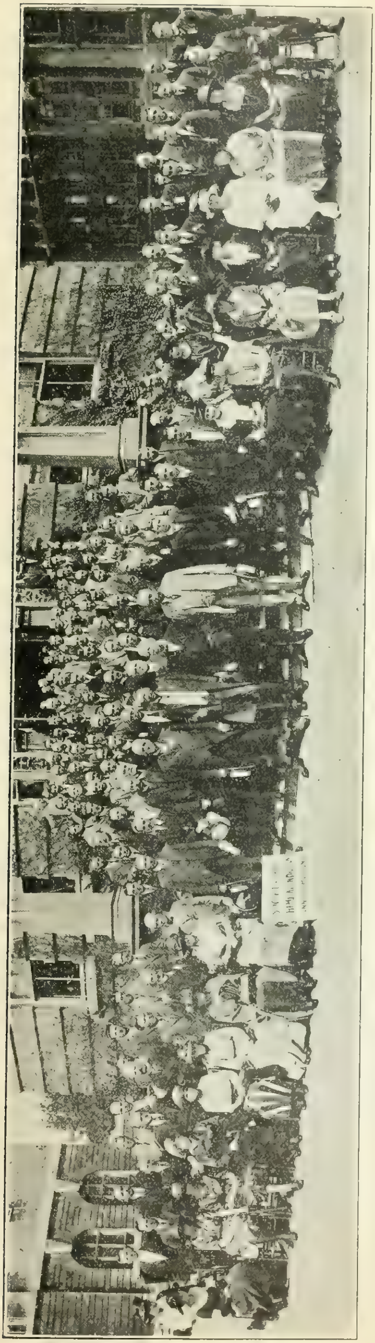
The Council unhesitatingly pronounced itself in favor of legislation for the protection of chemical scientific and illuminating glassware.

It was voted to hold the next meeting of the Society in Glasgow, Scotland.

President's Address

In his presidential address Sir William Pope traced the many activities of the Society of Chemical Industry and then discussed the question of how the chemical activities of the war period could be turned most effectively to the development of the greatest value in an era of peace. While recognizing clearly the fundamental importance of the accomplishments in the laboratory by synthetic organic chemists, nevertheless he pointed out the changed economic and political conditions throughout the world to-day as a result of the treaty of peace, whereby vast areas in tropical countries hitherto under the control of the German Empire had now passed, with the responsibility for their development, into the hands of British scientists. He emphasized the tremendous productive capacity of those tropical areas as a result of solar energy and called attention to the density of population in the temperate zones as compared with these tropical countries. Plainly, therefore, present-day conditions pointed to the greater utilization of that tropical solar energy and the development of organic material through cultivated crops, and the transportation of these products to the more crowded regions. Such a course seemed a more logical one for future effort than a close following of the method of the German laboratories which must work under such different conditions as to future sources of natural material. He was convinced that if anything approaching the amount of scientific effort previously devoted to laboratory research in synthetic organic chemistry should be devoted to increasing the yield of natural products and biochemical methods for their manufacture, there would be a great gain to the world.

On the evening of the opening day an important conference was held between the officers of the parent Society and the chairmen, secretaries, and treasurers of the Canadian and the American Sections. This conference, which extended over several hours, enabled a thorough discussion of many questions of policy and a careful mapping out of plans of extending the usefulness of the Society.



Group on Steps of the Chemistry Building, McGill University, Montreal, Canada, at the Close of the General Meeting during the Fortieth Annual Meeting of the Society of Chemical Industry, August 29, 1921

TECHNICAL SESSIONS

The morning sessions of August 30 and 31 and the afternoon session of August 30 were devoted to the reading of papers and to lively discussions. The following papers were presented:

TUESDAY, AUGUST 30, 10 A.M.

Need for Reform in the Education of Chemists. PROF. LASH MILLER.

The Problems Encountered in the Development of the High-Speed Paper Machines at the Laurentide Company's Plant at Grand'Mere and Their Solution. GEO. D. KILBERRY.

Action of Thiocyanate Solution on Cellulose. H. E. WILLIAMS.

Moving Picture of the Manufacture of Paper and Wood Operations at Price Bros.' Plant at Kenogami, Que., and Explanations. A. L. DAWE.

3 P.M.

The Properties of Pure Hydrogen Peroxide. O. MAASS.

Relative Density of Alkali Amalgams and Mercury. JAS. R. WITHROW.

Observations on the Chemistry of Rubber. G. S. WHITBY.

The Manufacture, Properties and Employment of Heat Intercepting Glass. GELLERT ALLEMAN.

WEDNESDAY, AUGUST 31, 10 A.M.

The Preparation of Synthetic Organic Chemicals. C. E. K. MEES.

Briquetting of Lignite. LESLIE THOMSON.

Peat and Its Preparation for the Market. ERNEST V. MOORE.

Theoretical Considerations on the Hargreaves Process. PROF. J. WATSON BAIN.

The Activation of Carbon. PROF. E. G. R. ARDAGH.

ENTERTAINMENTS

A feature of the meeting was the delightful luncheons, at which on each occasion a prominent Canadian citizen was present as a special guest. The luncheon on Monday was given at the Ritz-Carlton, and while the mayor of Montreal was unable to be present because of a conflicting engagement, he was ably represented by Dr. E. Dubeau, who possesses an unusual combination of titles, professor and alderman. Dr. Dubeau extended a hearty welcome to Montreal.

At Tuesday's luncheon the guest of honor was Sir Frederick Williams-Taylor, president of the Bank of Montreal, who gave an extended account of the natural resources of Canada, pointing out the needs of development in many lines.

The Wednesday luncheon group had as its special guest the eloquent Jacques Bureau, a member of the Canadian Parliament, who expressed the determination to do everything in his power to promote the furtherance of chemical research as the most certain means of ensuring Canada's future.

An automobile excursion to Ste. Anne's on Monday afternoon afforded opportunity to inspect the grounds and buildings and the facilities for experimental work in plant and animal husbandry at MacDonald College. After the tour of inspection a delightful garden party was held.

On Tuesday evening the annual banquet of the Society took place at the Engineers' Club. The large dining hall of the Club was filled with guests, and following the dinner a large number of speakers paid eloquent tribute to Canadian hospitality, discussed questions of policy, and testified to the necessity for closest coöperation between Anglo-Saxon chemists throughout the world.

McGill University formally conferred the degree of doctor of laws upon Sir William Pope. These ceremonies were carried out with impressive dignity on Wednesday afternoon, and the great audience was moved by the chaste address of the recipient in acknowledgment of the honors conferred upon him.

As a concluding feature of the session, a garden party was held on the campus of McGill University, at which many citizens were present and throughout which a spirit of cordiality and hearty good will showed clearly that the three days of close association had brought about that spirit of goodfellowship and mutual understanding which underlay the holding of the general meeting within Canadian borders.

CANADIAN INSTITUTE OF CHEMISTRY

During a part of Monday afternoon the members of the Canadian Institute of Chemistry held a business meeting of that young but vigorous organization in which Canadian chemists are now taking so much interest. Canadians have the disposition to hold their different opinions about subjects and to express these convictions unhesitatingly. To one who does not understand the Canadian temperament it would seem at times as if these tendencies might lead almost to riots, but upon gaining a closer touch and understanding it is readily noticeable that these differences leave no scars and are accepted as being honest and earnest efforts to contribute to the general well-being. Certainly it gets results. We were informed that this business meeting of the Institute was typically Canadian and we are convinced from the five-minute talks made at the dinner of the Institute on Monday evening, at which we had the good fortune to be a guest, that the Canadian Institute is growing steadily and healthily, that it has a distinct mission to perform for chemistry in Canada, and that under its present able leaders it is proceeding steadily toward that accomplishment.

The annual report of Secretary Roast showed 179 active members of the Institute, distributed as follows:

Honorary Fellows	1
Fellows	156
Associates	22

Provision has now been made for student membership. Active steps will at once be taken to develop this new feature of the Institute.

An employment bureau has been maintained by the Institute and the needs of its members carefully looked after.

EXCURSIONS

Late Wednesday evening an extended series of excursions was begun. Thursday was devoted to visits to Grand'Mere and the industries at Shawinigan Falls. On this portion of the trip the visitors were in the care of the Shawinigan Falls Section of the Society of Chemical Industry which continued in unabated form the spirit of hospitality shown at Montreal. Friday, September 2, was spent in a visit to Ottawa under the auspices of the Ottawa Section, while Saturday and Sunday were spent with the Toronto Section in visiting the various points of interest in Toronto and the journey across the Lake on a very uneven keel to Niagara Falls. Here the visitors were met by representative chemists of Niagara Falls and Buffalo and members of the American Chemical Society. Governor Miller had expected to be present to extend a welcome to the State of New York. He was unavoidably absent, however, and as his representative a most hearty welcome was extended by General J. Leslie Kincaid, Adjutant General of the State of New York. After inspecting the Falls and the electrical developments, the party moved on to Buffalo, where a motor trip over the city and in the evening a banquet at the University Club were given. The toastmaster at the banquet was Mr. W. H. Watkins of the National Aniline & Chemical Co. Addresses were made by Geo. S. Buck, of Buffalo, Dr. David Wesson, president of the American Institute of Chemical Engineers, Sir William Pope, Dr. James P. Longstaff, of London, secretary of the Society of Chemical Industry, M. L. Davis, of Toronto, Dr. W. A. Noyes, former president of the American Chemical Society, and Dr. John D. Wells, of Buffalo. All of the speakers emphasized the necessity of the closest possible relations between the British and Americans.

Much enthusiasm was aroused by the reading of a telegram from President Warren G. Harding to President Edgar F. Smith of the American Chemical Society (printed on page 873 in this issue).

From Buffalo the excursion was continued to Syracuse, where the party was met by officers of the Solvay Process Company and conducted to the plants of that company. After inspecting these, luncheon was tendered by the company and then the party entrained for Albany, from which point the night boat was taken to New York City. Throughout the entire trip the comfort of the visitors was constantly looked after by Mr. Charles E. Sholes, representative of the American Section of the Society of Chemical Industry. Arriving in New York Wednesday morning, the round of activities connected with the Annual Meeting of the American Chemical Society and the National Exposition of Chemical Industries was begun by a luncheon tendered by the Joint American Committees in the Butterfly Room of the Pennsylvania Hotel. Informal after-luncheon talks were made by a number of those present, particular interest attaching, however, to the remarks of Dr. William H. Nichols, not only because of his presence in the dual capacity of past president of both the Society of Chemical Industry and the American Chemical Society, but also because of his announcement of successful inauguration of the work of nitrogen fixation in America. Dr. Nichols said in part:

> We welcome our visitors from overseas and over the border with all the warmth that long association and friendly intercourse naturally produces. We congratulate our British friends on the intelligent and wise manner in which their government has coöperated to make the establishment of a great dye industry a certainty. The Germans led the way in close coöperation between the government and the industries, which made the German organic chemical industry what it became, and your government has shown in like manner its determination to do whatever may be necessary to make that industry, vital both in peace and in war, so secure with you that in the future you will be absolutely self-contained. We over here have strong hopes that our Congress will give us like assistance, so that the great industries forced upon us by the necessities of the war may continue and expand, and place us here also in the unassailable position which the talent and ingenuity of our chemists, and the almost limitless resources at our command will assure.
>
> Last night at the dinner following the Council Meeting of the American Chemical Society, I had the good fortune to sit next to our friend Dr. Bancroft. In the course of our chat, he asked me if anything new in the chemical world had come to light during the year. I reserved my reply until now, knowing that you also would be interested. I venture to say that a very great thing has been accomplished. At a meeting such as this, it would be a waste of words to discuss the importance to our country of the fixation of atmospheric nitrogen. Without having solved that problem, Germany would not have gone into the war, or could have sustained herself six months if she had. I am happy to announce that a subsidiary of the Allied Chemical & Dye Corporation has solved the problem for this country, and a plant has been running for some time to the entire satisfaction of the inventors and the Company. This country can therefore rest assured that this vital question need give it no further concern, except in so far as improvements in methods and engineering shall be the outcome of experience. No chemical engineer is satisfied with what he accomplishes but is always striving for something better, and of course it would be surprising if what has been accomplished here should not be improved upon very greatly. I feel assured, however, that what we have constructed here and are now operating has been better done than anywhere else hitherto. I cannot tell you how much pleasure it gives me to make this announcement at the end of six or seven years of painstaking research engaged in by a large staff, interrupted as it was by the necessities of the war.
>
> I feel sure this announcement also gives pleasure to our visitors from across the sea, whom I know to be big enough to appreciate good work wherever done.

……

This luncheon marked the fusion point of British, Canadian, and American chemists. From that point on, all participated alike in the various meetings of the American Chemical Society and in the many activities of Exposition Week. To return to the figure used editorially a year ago, the process of rope-making was so complete that the individual strands could scarcely be detected.

Great is the strength thereof.

ANNUAL MEETING, AMERICAN CHEMICAL SOCIETY

From the Tower

The concentrated chemical activities of the three weeks of 1921 are now history. True, this history is of such recent making that it is difficult to get the proper perspective to give correct values to the several events of this interesting period, but certainly it is worth while, even at this early date, to ask ourselves frankly, "What does it all signify? What will be lasting, what ephemeral?"

We can only record our share of the answer by contrasting the feeling which almost overwhelmed us with depression in midsummer with that which now buoys us with confidence. The action of the House of Representatives in rejecting the limited selective embargo feature of the tariff bill was a wet blanket, we confess. It indicated an attitude of indifference, nay, almost of such antagonism to chemistry as characterized the War Department in the early days of the war. But the latter fight was won and by the tokens of these last three weeks, Congressional support will finally be won. The message of President Harding, read at Buffalo, was the initial factor in inspiring confidence. This was followed by the fearless and thoughtful address of Mr. Garvan at the opening meeting, and the closing address of President Smith, brimming over with purest patriotism. The enthusiastic unanimous vote of the General Meeting on the resolutions urging favorable legislation by Congress left no doubt as to the opinion among chemists on this subject. Then came the straightforward address of Senator Lenroot, who brought with him constructive suggestions, and that of Congressman Purnell, who urged greatest possible protection for our dye industry.

Intermingled with these events were constant opportunities to meet in friendly personal acquaintance our fellow chemists from England and from Canada, gaining thus the wider aspiration and the deeper determination ultimately to gain success. Lasting evidence of the close union of those who lately worked side by side on questions of war was the conferring of honorary membership in the AMERICAN CHEMICAL SOCIETY upon Sir William Pope and M. Paul Kestner, the leaders of the organized forces of chemical industry in England and in France.

There was a thrill of unusual feeling at the opening meeting in Montreal; it showed itself in a wave of enthusiasm at the New York Meeting; and it was reflected in the outpouring of a deeply sympathetic public during the week of the Exposition. What better sign of this popular interest could be asked than was furnished by the press of the country, which devoted so much space to well-written accounts of the proceedings, together with thoughtful editorial discussion.

There was a notable assemblage of distinguished personalities at the International Meeting and its full significance and importance will grow as the days go by.

The divisional meetings were largely attended, the papers presented exceeding any previous meeting. Discerning criticism will separate the sheep and the goats on these programs. Undoubtedly there were some goats.

It is interesting during the week of a General Meeting to watch the development of the spirit of such a gathering and to try to interpret that spirit in a few words. At Chicago it was a determination to maintain the unity and solvency of the SOCIETY; at Rochester it was a spirit of confidence and boosting; at New York it was conviction as to individual responsibility for awakening the Nation to an understanding of the potentialities of chemistry, and a determination to meet that responsibility.

Council Meeting

Rumford Hall, Chemists' Club, was the gathering place on Tuesday afternoon, September 6, 1921, of the largest Council Meeting in the history of the SOCIETY. President Edgar F. Smith was in the chair, and one hundred and sixteen councilors were present in person or by proxy. The business of the day consisted in large part of matters concerning the internal policies of the SOCIETY, a complete report of which will be found in the Proceedings in the October issue of the *Journal of the American Chemical Society.*

Two matters of national policy were discussed at length. The SOCIETY'S Committee on Patents and Related Legislation submitted a report on the Stanley Bill, S. 1838, now before Congress. In connection with the ensuing discussion the following resolution was unanimously passed:

> While the Council is disposed to accept the views of its Committee on Patents, nevertheless it is felt that a constructive suggestion should be made by the Committee as to legislation which would prevent the utilization of our Patent Office by foreigners for the suppression of the development of industries such as was so clearly apparent in the organic chemical industry upon our entrance into the war in 1917. The Committee is therefore urged to consider this problem immediately and to report to the Committee on National Policies.

President Smith outlined the present legislative situation with regard to the organic chemical industry, whereupon it was moved that resolutions urging the passage of a limited embargo on synthetic organic chemicals be prepared for presentation to the General Meeting on the following day.

It was decided to hold the Annual Meeting in September 1922, at Pittsburgh, Pa. It will be remembered that this Section very graciously relinquished its lien upon the September 1921 date to permit the international gathering to be held in New York City. The Spring Meeting will be held in Birmingham, Ala., early in April 1922.

The Sections of Sugar Chemistry and of Leather Chemistry were granted divisional status. It was voted to withdraw the charter of the South Carolina Local Section, which has not held a meeting for several years.

The Secretary presented an ad interim report of the Finance Committee and gave statistics regarding the paid and unpaid membership. It is estimated by the Directors that the actual expenditures for the year 1921 will exceed the receipts by approximately $10,000.

The Committee on the Amendment to Article 13 of the Constitution, allowing an increased pro rata apportionment to local sections, reported adversely in view of the present financial condition. The matter was laid upon the table until the next annual meeting.

The president of the Chemists' Club, John E. Teeple, presented a suggestion that the SOCIETY take over the Bureau of Employment now run by the Club, or establish a bureau to replace this organization. In accordance with the Council vote, the President appointed a committee consisting of H. P. Talbot, Edward Bartow, and A. C. Fieldner, to consider this question and report at the Spring Meeting.

Dr. Smith told of the work of the Priestley Memorial Committee, describing the Priestley portrait, and outlining the plans of the Committee to establish a Priestley Medal fund. Plans are also under way for the restoration of the Priestley home at Northumberland, Pa., and President Smith spoke feelingly of his wish that the SOCIETY might celebrate its fiftieth anniversary with a meeting at Northumberland in 1925.

Following adjournment the councilors took dinner at the Chemists' Club, as guests of the New York Section.

Story of the Week

General Meeting

About one thousand members and guests had gathered in the spacious gymnasium of Columbia University for the first session of the sixty-second meeting of the American Chemical Society, Wednesday morning, September 7, when Dr. John E. Teeple, chairman of the New York Section, began his address of welcome. The British and Canadian visitors arrived during the course of the meeting. Before the end of the week the total registration had reached 1557. Dr. Teeple's address follows, in part:

Address of Welcome

By John E. Teeple

Twice each year, it is the great pleasure of some one of the sixty sections of the American Chemical Society to welcome as its guests the members of the other fifty-nine sections assembled in general meeting. This year it is my pleasant duty, on behalf of the New York Section, to extend you this welcome, to offer you the keys of the city in so far as the keys may be in our possession or as they may be required in such an open town as New York.

Our British friends sometimes accuse us of an undue use of superlatives. At the risk of meriting this accusation let me say that this will probably be the largest gathering of chemists that has ever attended any meeting of our Society, which Society is the largest chemical organization in the world. Yet size alone is unimportant, excepting as an index of the interest in and the character of the work, and we hope that this meeting will be remembered not for its size but for the quality of the papers read, the discussions, and for the inspiration received when such a body of specially selected men gather to discuss their one problem from many points of view.

This one problem that chemists have in common is the transformation of matter, the making over of the resources of the earth into forms of matter suitable for the use or the development of man. Our brothers in science and its application, the physicists and the engineers, can do wonderful things in the erection of buildings, bridges, railroads, telegraphs, and means of locomotion and communication, but their hands fall absolutely to their sides unless the chemists can furnish them the materials of construction necessary, the iron, steels of many kinds, the alloys, and the other metals of various kinds. No one of these materials exists in nature in a form suitable for their use. In every case we must take something that nature furnishes and transform it by chemical processes into something else which is suitable for construction material.

The world is only to-day awakening to the importance of the chemist and his work, and we are proud, very proud, to have a part in the science and the practice of chemistry.

For untold generations man lived on earth with no knowledge of chemical changes. He could form matter and shape it and adapt it, but he could not change it. He could polish a flint or carve a bone, but it was still only a flint or a bone. Great landmarks of his progress in civilization stand out as the points where he discovered that he could control chemical changes. When he first reduced iron oxide to iron he added an entirely new and valuable raw material to the world that had never existed before. When he converted vegetable fiber into paper, or sand and soda and lime into glass, he was increasing enormously his possibilities of development.

We are gradually mastering nature. New products are now coming so fast we can scarcely keep abreast even of the records of their discoveries. It is a very great privilege to have a part in this work of mastery.

After responding to this hearty welcome, Dr. Edgar F. Smith, president of the American Chemical Society, introduced Francis P. Garvan, president of the Chemical Foundation, whose stirring address is given in full below:

Chemistry and the State

By Francis P. Garvan

"Nothing can be more certain than that the character and rapidity of our national development in all matters which relate to *industry, agriculture, public health and the preservation of the physical framework of our civilization* will be dependent upon the quantity and quality of sound research which is carried on. The truth of this assertion becomes even more apparent when one recognizes the fact that every modern nation stands in relation of industrial and commercial competition with other nations and in the measure in which this is true, to fall behind the others in scientific development is to *precipitate* a trend of events which spells national depression and disaster. In other words, the price of a sound, comprehensive national life is, in these times, widespread and intelligent scientific research." These are the words of Prof. Angell, the new president of the new Yale University. But President Angell stopped halfway.

Pasteur thought it through when he said: "In our century science is the soul of the prosperity of nations and the living source of all progress. Undoubtedly, the tiring daily discussions of politics seem to be our guide—empty appearances—what really leads us forward are a few scientific discoveries and their application."

Courtesy Pirie MacDonald

Francis P. Garvan

But sound and comprehensive scientific research and a practical development of the application of the results and discoveries of such research is impossible in any country, without an appreciative understanding of the truth of these two quotations by the peoples of that country, reflected in their educational system, their business development, their governmental guidance and, if necessary, control and supervision.

These two quotations express, in my opinion, the truest appreciation of the cause of the war and point out to us its chief lesson. But more than that, they throw upon your shoulders as chemists the great responsibility of seeing to it that that lesson is learned and applied by your respective states.

Public Trusts the Chemists

The reputation for honesty and disinterested truthfulness of the chemists of the three nations joined here to-day is so well established and recognized that only from your lips will the peoples of our different countries accept the truth of these propositions.

Economists like Hauser, Lord Moulton or Angell may thunder these truths. Historians, cold or imaginative, like Balfour, Wells, Irwin or Simonds, may present in startling form their conclusions or prophecies, but a war-weary world hesitates to adopt their conclusions.

You and you only do they trust, and progress and safety place the heavy responsibility upon you of making chemistry, its aims and possibilities, understood by public schools, high schools, universities and post-graduate schools, by industry and agriculture, and by the representatives of the people in municipality, state and nation.

The people of the United States are ninety-nine per cent right at heart and appreciative; so are the people of England and of Canada. Their appreciation of chemistry must no longer be defined in the terminology of the propaganda of foreign hostile interests seeking only their destruction.

Your work must never again be allowed to cease in the laboratory.

The discovery and its application which to-day is only the latest proof of the truth of Pasteur and Angell occurred in 1856. In that year, your fellow Englishman, William Henry Perkin, aged eighteen, while engaged in scientific research in a laboratory in London, having for its object the artificial production of quinine, obtained a muddy dark precipitate which, washed in alcohol, proved to be the dye we call mauve.

This discovery, with its principles, has been the basis for all the subsequent development of the coal-tar industry and practically of all organic chemistry.

His efforts met English industries without understanding; met a public and a government without appreciation, and fellow chemists without a realization of the responsibilities of directing and enlightening English thought.

The German Hofmann put the discovery in his bag and took it back to Germany. Almost instantly, he, and he typifies his chemical successors, was able to make German industry, German universities and the German government realize the importance of the contents of that bag.

A TRIPLE ALLIANCE

Immediate success led to a greater appreciation of an ever-closer alliance of science and industry, and an ever-closer alliance between science, industry and the militaristic state. This triple alliance changed Germany from an agricultural nation into the second industrial nation of the world, but in that change, it brought about a succession of periods of over-production, each one in turn overcome by greater consolidation, by ever-increasing corruption in methods of bribery, espionage, dumping, et cetera, and by ever-intensified state aid and direction.

In 1914, we find the German people demanding the control of the markets of the world. We find their hearts corrupted by the methods which they had felt it necessary to adopt to overcome their successive periods of over-production. We find them swollen with pride at their successes and ready to inspire or acquiesce in the hazard of battle. This triple alliance of industry, science and the militaristic state—and the evidence is overwhelming that each was equally guilty—considered that it would be quicker and cheaper to attempt to gain this end by victory on the field of battle, rather than to find increased markets for a surplus production by further intensified methods of peaceful penetration.

The same chemical research with its well-served industry had in turn well served the militaristic state. As chemical progress indexed commercial progress, so explosives had kept pace with dyes and pharmaceuticals, the ammunition factories of her peaceful penetration were the arsenals of her munitions preparation.

In the fall of 1913, the chemical application of Perkin's discovery was able to notify the war lord that Germany was ready; that she controlled 95 per cent of the organic chemistry of the world upon which industry and the production of explosives were dependent; that she had crushed out every incipient effort toward the development of the Perkin discoveries by every other nation and was able to deal the dependent industries of those nations tremendous blows, and that now by the final triumph in the development of the Haber process of making nitrates from the air, her agricultural production and munition production were safe from the menace of any blockade.

You know the rest.

All this German chemists accomplished not alone in their laboratories but in the forum of public opinion. They had educated and molded thought in Germany until every man of whatever rank, in or out of industry, education or governmental service, realized the importance of chemistry in his life and in the life of his country.

WORLD'S WEALTH INCREASED

They knew that the alliance of science and industry had increased the wealth of the world a thousand-fold in the past hundred years.

They knew that it was the life-blood of industry; they knew it was the safety of their state and the only sure foundation upon which to base the hope of the health of their children and their children's children, and they had impressed upon the world the discouraging and withering idea that the Germans and the Germans alone were mentally equipped to lead in this great age of chemistry.

You may answer me that I reproach you with results which could not have been foreseen, but I tell you that for three years I have been reading the records and the correspondence and the private papers of German chemists, German business men and German Imperial representatives, and I have been forced to realize that every result had been foreseen, realized, appreciated and worked for by every chemist in the German nation.

Just one or two instances: Prior to 1908, German patent laws contained the so-called working clause, by which your inventions, if patented in Germany, must be worked there within a certain period of time or they were thrown open to the German manufacturers and developers. Agitation was rife in this country that we should protect our future in like manner.

But by 1908 Germany had decided that she had so far advanced in science that she no longer needed that clause to protect herself and that if enacted by the United States it would threaten her control of organic chemistry in the world and destroy the purposes upon which she was bent.

The president of the Bayer Chemical Company, at that time the head representative of this march for world control in America, although on paper an American citizen, acting under instructions from the consolidated government and chemical industries of Berlin, went to Commissioner Moore at the Patent Office in Washington. It was the beginning of one of Washington's hot summers. With fulsome praise of his outstanding position in the patent world and the great inventive genius of this country needing protection, he reproached him for not representing the United States at the International Patent Conference about to be held in Stockholm. Mr. Moore responded that the unenlightened Congress had not given him any funds with which to go. Mr. Moore then went on his vacation. Mr. Muehling, the predecessor of Schweitzer and Metz as the American voice of Germany's chemical interests, went to Robert Bacon, then Acting Secretary of State, drew the picture of the United States unrepresented at that great Conference, pointed out to him that he had a fund which he could apply to any purpose which he deemed for the best interests of the country in its foreign relations, with the result that Mr. Moore was recalled from his vacation and sent abroad; but with him went a letter to the German chemists, telling them that the American representative of the German dream had done his part and that they must now do theirs.

THE GERMAN PATENTS

The result was that Moore was induced to go from Stockholm to Berlin, where he was fêted and dined by the Kaiser himself and returned to negotiate the Treaty of 1909 with Germany, by which Germany was released from ever working her chemical patents in this country and by which the last hope of development of organic chemistry in this country was crushed.

No more loyal Americans ever lived than Robert Bacon and Commissioner Moore, but they were unconscious tools in the hands of the German chemists, the handmaidens of the German dream of world control. And you were to blame, because you had not instructed your government officials up to a realization of the importance of chemistry and its guidance and protection by the state.

When the war broke out in 1914, four billion dollars of annual industry in this country, to say nothing of our physicians and hospitals, were dependent upon the will of the German Emperor as exercised through six importing firms and about four mere assembling plants. At the Kaiser's nod he summoned their assistance.

Listen! April 25, 1915, Boy-Ed writes to Albert:

> Very Honorable Privy Counsellor:
>
> Today's *World* prints the enclosed short article on the alleged erection of dye factories in New Jersey by Germans. In case you are not able to take any steps to prevent an undertaking of this kind, I am requesting you to indicate to whose attention I could call the matter.
>
> With greetings, etc.,
>
> (*Signed*) BOY-ED

Albert answers, April 28, 1915:

> With regard to dyes, I got in touch with local experts in order to determine what truth there is in the news. According to my knowledge of things, the matter is a fake, inasmuch as our factories have bound themselves orally and by word of honor to do nothing in the present situation which might help the United States.

As a result, Bernstorff was able to cable his country that they had in their possession the weapon by which four million men in this country could be instantly thrown out of work, as an argument why America should attempt to force England to lift the blockade.

DRUG SUPPLY CUT OFF

As a result, the German government did issue an order, only to be met by a final realization of your own intrinsic ability. As a result, Germany was able to shut off as a further threat the supply of salvarsan and luminal from this country, which in her heartlessness she did, leaving thousands of epileptics and ten million syphilitics without any relief from the ravages of that plague and consequently menacing the other ninety millions of our people.

I could go on pointing out the results, but it is not necessary.

But why dwell upon the errors of yesterday?

The situation is as acute to-day as it was in 1908, in 1910, in 1914, or in 1916 and 1917.

Yes, the war is over, but the situation is the same.

This was an industrial war, brought on by industrial Germany in her lust-mad haste to capture the markets of the world. Industrial Germany, in her arrogance and pride, preferred the formidable hazard of battle to the progressive and sure infiltration which within ten or twenty years might well have given her the world domination she sought from complacent and unthinking people.

Her ambitions are the same to-day as they were in 1914. Her methods are the same in peace and war.

Through the most extraordinary coalition of Science, Industry and Government that the world ever saw, Germany in the past leaped leagues ahead of rival nations, and as she ran she found means to clog the feet of her competitors.

Rapidly recovering from the debilitation of war losses, Germany is once more driving ahead in this special and all-important field. Once more she plans to deceive her rivals as to the importance of this special key industry of chemical production. Again she tries to clog the feet of competitors.

Once more she sends her spies and agents to this country and reinspires Germans, camouflaged as Americans, to poison the well from which America should draw her full strength for peace or war. Can that be done successfully here and in England and France, Germany will be a menace to world peace within a decade.

It is our people, our statesmen, she seeks to lull and benumb. Let her gain her end and she will have developed within ten years, from her experience in the Great War and through the magic of her doctors of chemical research, through her tremendous and closely welded chemical industry under government protection, from her intensified alliance of Science, Industry and Government, peace weapons and war weapons of potency unforeseeable.

A MIGHTY WEAPON

We have in our grasp to-day the means to make the United States forever independent in peace and war. In our grasp are the essentials for the control of disease, for the vast increase of food production, for the immense development of domestic and foreign industries, for secure national defense. We have universities ready to supply us with the personnel to put us in the forefront in this chemical age.

Are we so unconcerned, so dully perceptionless, so stupidly asleep that we will permit German intrigue to stifle this priceless acquisition, which has cost us millions of dollars and twenty-seven per cent of our war casualties?

Do we think that we are at peace because our Government has formulated a set of words declaring that peace exists, and because our President has put his signature to the document? Fatal assumption!

With the German people, dominated by their ineradicable mania of superiority, the war has passed into another stage merely. But it is the same war, waged with new weapons.

All the defeats and punishment suffered by Germany from 1914 to 1918 were invaluable discipline and experience for continuing the indecisive struggle.

Germany was not conquered. She was merely stopped, thrown back for a time. She did not experience the agonies of invasion. Her people did not groan under the horrors that fell upon Belgium, France, Rumania and Russia. Never forget that the German people greeted the baffled German armies as the Romans were accustomed to salute the legions of victorious Caesar. The retiring hordes, flowing back into the Fatherland, were garlanded with flowers. The incidents of roadway and city square as the gray-green warriors fell back before the menace of Foch, Haig, and Pershing cry with shouting tongues to thoughtful men. A subdued people, a people conscious of defeat, do not crown their unsuccessful legionaries with laurel and jasmine.

Their attitude shouts aloud the set purpose of the German mind to begin anew, patiently, devotedly, in the silence of their laboratories their task of dominating a world so ridiculously inferior to themselves.

If this were mere speculation, I would waste neither your time nor my own; but my assertions are buttressed by timbers of hard fact.

In Germany to-day industrial reorganization for world domination first in the peaceful arts and then in war is proceeding mightily under the sympathetic eye and fostering care of a government which differs in no important particular, so far as the world outside of Germany is concerned, from the government of the Hohenzollerns. The German purpose stands forth as clearly as a mountain in the sunlight: First, reconquer in industry and commerce, then we Germans will see.

Their secret documents prove it. The heart of the news that comes out of Germany proves it. They prove it out of their own mouths.

Moles in the darkness, German agents in America are once more plotting against our security, our prosperity and against the health of our very children. The German design to render the United States impotent is being prosecuted to-day with more subtle viciousness than marked the intrigue of von Bernstorff, Dr. Albert and Hugo Schweitzer in the years before we entered the war.

A Time of Danger

The times are too tense with danger for passive tactics. On one side we have the same old crowd of German agents masquerading as good Americans. On another side we perceive American citizens supporting the German intrigues. In Congress we hear and stand aghast at the ignorant and malicious outbursts of certain legislators, unmindful of their country's welfare. Folly drips from their mouths. Stupid suspicion of the motives of honest men and appalling ignorance of the times mark their astounding incapacity. There are some who, like Jacob of old, have set themselves to steal the birthright of chemical independence from the American nation. They may disguise for a time the hairy hands of the German dye monopoly that controls them, but in the end the people will know them for what they are.

Their voices are the voices of elected Representatives and Senators in the American Congress, but the hands that manipulate them are the hands of the German Dye Trust, the most powerful monopoly ever formed by man, the Interessen Gemeinschaft, the "I. G."

Joseph Frederick Naumann, German economist, editor, and member of the Reichstag, in the most successful and probably the ablest book that has appeared in Germany since the beginning of the war, "Central Europe," frankly admits this charge.

> The war (he says) was really only a continuation of our previous life with other tools but based on the same methods. In this, indeed, lies the secret of success * * * if our opponents like to label this intrinsic connection between war and peace "German militarism," we can only regard this as reasonable, for Prussian military discipline influences us all in actual fact, from the captain of industry to the maker of earthworks. * * * Happen what will, the German spirit has received its baptism of fire; the national genius was and is a reality. Both to ourselves and to the outside world we have shown ourselves as in essence a single unit. Now it is our concern to carry through to its goal this essential German character, proved in the most sinister of wars. This will and must be set on foot directly peace is concluded.

And a little further along:

> We shall enjoy our golden age as other conquering nations in other ages and with other abilities and excellence have done before us. Our epoch dawns when English capitalism has reached and overstepped its highest point, and we have been educated for this epoch by Frederick II, Kant, Scharnhorst, Siemens, Krupp, Bismarck, Bebel, Legien, Kirdorf and Ballin. Our dead have fallen on the field for the sake of our fatherland, Germany, foremost in the world.

Because the peculiar circumstances of my service to the United States gave me a most effective perspective of the German purpose of advancing German power while weakening American strength, I am driven to speak out. With the hope that this truth will stick fast in the national consciousness, I have the temerity to awake the lessons of the war and urge you to do your part toward awakening the American people before it is too late.

If, in the reaction of war and in the general distaste for discussing matters pertaining to war, we permit ourselves again to be lulled and numbed by German propaganda; if we look on indifferently while a few demagogs in Congress and a few shortsighted, selfish men in business life play the German game; if we allow Germany to stifle an American industry that would within a very few years make the United States absolutely safe, then, I say, it will have been through your neglect and temerity and failure to realize that it is your responsibility not only to search the truth, but to preach it.

A Greater Responsibility

Your responsibility to-day is the same as it was during all these years of neglect, only intensified as it must be by your consciousness of the results of that neglect.

You alone in your town or village can see to it that these truths are realized by public school and high school; you alone in your state can see to it that these truths are realized by universities and state legislators in control of education.

You alone can see to it that in the National Government, your representatives in Patent Office, in Bureau of Education, in State Department and in Congress are kept abreast with your development and needs, that every insidious attack is exposed and refuted.

You must be mindful of the fact that most of our school heads, our great editors, our government officials, both administrative and legislative, have been educated in what one of your English compatriots has called "Museums of Ancient Learning" and that the war has for the first time and but partially, opened their minds to a realization of the scientific progress of the last century and its true relation to national progress.

Are you awake? I do not think so, with the exception of a few. You have listened without apparent protest, contenting yourselves with resolutions and telegrams, both good, but not sufficient to controvert the German lie that there was a "Dye Monopoly" in this country, or that such a monopoly would result from the enactment of a selective embargo, when you knew that the development of a dye industry is synonymous with the development of education in organic chemistry and that no monopoly in education is possible without the compulsory partnership of industry, university and government, such as exists in Germany. (A monopoly which never worries those tools of German propaganda.)

You knew that Senator Frelinghuysen spoke the truth when he pledged his honor on the floor of the Senate that there were already forty-six independent dye concerns in his own state, and the Senators from this Empire State, when they find their voice, can stand up and say that there are twenty-nine more here.

Not a "Dye Fight"

I say you have heard it called a "dye fight," when you knew it was a fight of organic chemistry; when you knew that "dyes as dyes" do not in normal times constitute a gross business of more than $40,000,000 a year, not as much as our children spend in toy balloons, or our five and ten cent stores take in in a month

You heard without audible resentment the German lie that the Chemical Foundation was another monopoly and had purchased, for less than their value, patents belonging to the innocent men of Germany. You knew that no stockholder, trustee or president ever has made or ever can make a penny out of the Chemical Foundation; that it was formed to represent the American people in their purchase of their freedom from the clutch of the hands seeking to misuse the beneficence of their laws to choke our industrial development, our means of defense, and our hope of the preservation and conservation of the health of our manhood and womanhood.

You know that the U. S. Constitution gave Congress power to issue patents in order to offer inducement to the publication of each successive discovery in science, in order that it may be made the stepping stone for future progress, and you know that practically all German patents were taken out with the intent to conceal and suppress advance in scientific information and what the Foundation bought was useless, unless American business spent millions of dollars to find out the necessary information which the patents concealed.

You knew that the attack on the Foundation was a German attempt to diminish the usefulness of the organization which they know will never quit until every man, woman and child in this land knows the whole hideous past chemical story and has a vision of the wondrous future of chemistry in the idealistic hands of the Anglo-Saxon race.

It was only freedom from blackmail and the consequences of imbibed German propaganda intended for our destruction that the Foundation bought. All other nations accomplished the same result without any compensation to Germany.

What would they? Should the American Government give back to the Germany, which in 1915 attempted by the use of her patents to throw four million American citizens out of work, in order to blackmail our Government, the right to do so now for the purposes of her peace-time conquest of the world's markets?

Would you have the American Government hand back the patents covering the only weapon with which we can fight the dread scourge syphilis, to the country which once shut off our supply while we were at peace with her, to further her war-time purposes, without assurance greater than her word, greater than her scrap of paper assurance, that an attempt to use the same power would not again be made to accomplish some one of her aims?

Germany and Congress

Did it not bring to your minds the lessons of the war when you saw the importing representative of the German "I. G." stand on the floor of the House of Representatives, flanked by fifteen of the seventeen Congressmen who voted against the declaration of war, leading the cheering when the first great unsuccessful test came as to whether American chemists should be given a chance to catch up their neglect of forty years and atone for it by leading this country through the development of organic chemistry into the realms of intensified national industrial progress, sweet security to home and child, and blessed advance in the medical service of humanity? Do you not feel that the voices of two German importing firms were louder in protest and more persistent in their appeal for Germany than the voices of your fifteen thousand members for America's lessons of the war.

Again I repeat, Herman A. Metz stood upon the floor of the House as that vote was announced and shouted to a gallery of American citizens, "I've got you licked." And when he screamed in triumph, he meant "I, the representative of the Interessen Gemeinschaft, the 'I. G.,' the combination of German government and German chemical industries; I've licked the advice of your General Pershing; I've licked the advice of your Secretary of War; I've licked the advice of your Secretary of Navy; I've licked your President; I've licked your Administration; I've licked your thirty million dollars investment in your colleges; I've licked your chemistry in your high schools and your public schools; I've licked your research institutions and the future development of medicine in America."

Chemistry in the Colleges

Motives of politicians are questioned, interests in industries are antagonistic, but your heritage, the purity and spotlessness of your great white plume insures you attention and burdens you with the responsibility. Each in your own community must tell the story of chemistry to the Boy Scouts and the Rotary Clubs, the school boards and the public and high school teachers, the local editors, clergymen, and physicians. You can point out how chemistry can serve each of your local industries, the agriculture of your community and the public health of your city; and more than all, you can meet and refute, not only the false ideas which have been inculcated in the past by German propaganda, but each new lie which her system puts forth. The universities have already harkened to you. The study of man, his emotions and the tongues and learning of the dead past, last sanctuaries of lost causes, are already being forced into their proportionate place in the curricula, and the understanding by man of the world in which he lives and his relation to it is being given its proper importance. In this country, during the past year, over thirty millions of dollars have been appropriated by the different universities to the promotion of the study of chemistry. For instance, Yale has appropriated three and one-half millions to build the finest laboratory in the world, and has also established chairs of research, whose occupants will be free from the labor of teaching. Harvard and Princeton are about to follow suit; Cornell has appropriated five hundred thousand dollars; so it is right straight across the country. I need only mention that great research institutions are springing up, such as the endowment in Leland Stanford, for research studies in the chemistry of foods, and a great, as yet unnamed, philanthropist is establishing a wonderful institution to insure in this country the proper research into the chemistry of plant life. This phase of the situation is most encouraging.

But most of our representatives in the executive and legislative branches of our states and of our nation are graduates of universities of the past, and their experience, as my experience, with chemistry and science in general, is as yet a closed book to them, and it is for you to supply to them the true information, to enable them not only to safeguard our progress by encouraging and fostering legislation, but also to prevent them from being influenced by information at the hands of your enemies.

To Eliminate War

You can tell them and they will believe you, at least 99 out of 100, for they are honest men, that your science is the life blood of industry, eliminating waste and purifying the products of the soil, of the mine and of the factory. You can tell them that there has come into the world a realization that the empirical system of medicine has reached its limit, and that chemistry is ready to join hands with medicine and physics, in eliminating the waste of disease and in intensifying the vigor and strength of our people, and then you can talk to them about war.

They will not believe the imagination of a Wells or the prophecy of Will Irwin, but you know and can tell them that with twenty years of progress, if progress there is to be, by great and small nations of the world in the study and development of chemistry, *war will be unthinkable.*

The thrilling picture painted by Wells of the appalling destructive persistency of radioactive elements and of the awful hopelessness of defense against such forces, is as definitely prophetic as Jules Verne's vision of the submarine or Rudyard Kipling's description of the swooping flight of the night mail flyer from London to Quebec. Inspiration of men of letters raised high above the weights of fear and superstition and dull habits that clog trammeled imagination lifts them to regions where they are fired by whispers of hidden things.

The creative chemist to-day is their blood brother in unappeasable imaginative effort. The world of his dreams is the scarcely touched sources of natural force, and the goal of achievement to which he has set his face as he toils against the heartbreaking road that all must tread who dream of benefiting the race, is the absolute mastery of man over nature. Wittingly they weave their webs and wittingly they set the snare that will some day catch the sun, as Wells puts it.

Our research chemists know as certainly as they comprehend the relationship of the molecules they take apart and put together, that human beings will not cease fighting each other and killing each other until the game is made too frightful for imagination to contemplate.

Ancient Pacifists

They do not believe that war can be stricken from the list of man's evil practices by appeals to his better nature or by reasoning with his intellect. For men have been slaying each other from anger or self-interest since the time when the first hairy males hated the animal scent of each other, or coveted each others' females, or quarreled to a deadly finish over the raw flesh of a mammoth trapped in asphalt bogs. Even in that remote time, there must have been a few gentle souls, among the very old; among the few that had caught a gleam of the glory of life, who pleaded in strange, guttural eagerness for milder and more tolerant ways. Such doubtless were clubbed to death by their incensed sons, or driven from the fire to perish in exile. The clucking first men peace advocates of 20,000 years ago, scarce daring to raise rude gutturals of protest against the murder and rapine done by their brute-like sons, were few and fearful creatures we surmise; but their kind has increased marvelously since mankind has learned through suffering of his own making to think more clearly than the brutes around him, and to-day there are millions of protestants against war where one dared to speak out a few centuries ago. The idea that war is a crime instead of a glorious sport has taken hold of peoples according to the degree of their experience and their intelligence.

The comprehension that it is nothing but an appalling wastage of the toil of generations, that it is altogether brutalizing without a single compensatory side, is surely penetrating our thick minds. Bitter experience that the wastage and destruction of war is not confined to a period of warring but that they persist through miserable after-years, is getting home to our understanding. The vast majority of human beings alive to-day would give thanks to the variously named Supreme Being, if they could but know that the legalized, wholesale murder called war was done for, finished. We are perfectly sure that this is so. Why, then, does not man end it once and for all? Why, knowing the better, does he continue to practice the worse in double guilt?

Perhaps we find an answer to this speculation in the tracery of the development of the peace idea. Put it squarely; peace advocates have multiplied and the peace idea has spread in singular relationship to the killing, searing, burning, mangling, poisoning, mass-destroying development of war weapons. As warfare has slowly grown more terrible, so men have turned slowly but in greater and greater numbers to peace hopes and peace plans.

Chemistry and War

As struggles between nations became more destructive, not only in actual warfare but in the paralyzing blows delivered to peace-time industry, more and more came to kneel at the altar of peace. When war science learned how to destroy thousands at a stroke, to ruin whole cities in the space of a breath drawn in the middle of the night, peace seemed more and more desirable.

As the researchers in the sciences contributed in ever-increasing frightfulness to the power and long distance application of war weapons, destroying all the romance of industrial combat and nullifying individual courage, men began to see increasing merit in the dreams of those who would abolish war utterly and who would police the evil doers of the earth as such are policed in our cities.

When the creative chemist showed military commanders how an opposing host could be stricken from life on the wings of the wind, laid horribly in death by a vapor as noiseless as the pinions of Azrael; how life could be expelled from great cities by a death dew of acids sprinkled from invisible airplanes, peace became a boon to be prayed for in utter sincerity. Hypocrisy smiling at gunpowder blanched before phosgene gas.

Peace is much more popular now that men know how to destroy each other with cotton in the form of nitrocellulose drawn from the air, than when they abolished each other with cellulose in the form of a club.

I do not say that the spread of education and gradual refinement of the spiritual side of man has not played a part in the growth of the ideal, or that the operation of pure reason has not contributed to the vitality of the desire.

I do maintain with history at my back that successive inventions of horribly destructive weapons and successive demonstrations of the magnified and unpreventable ruin and misery wrought by one new weapon after another, have been successive shocks to man's long-time notions about the indispensability of war.

There was a time when he said that war could not be prevented. Then he began to say that it was disagreeable on the whole, that it ought to be prevented. Now he is beginning to see that it is so frightful that it *must* be prevented.

Until a day in April six years ago his dislike for war was never so intense as to make him pause to think deliberately before he plunged into it. Until April 1915, his fears for his personal safety and for the safety of those he left at home was never so overpowering as to make him say, "I dare not begin." Great guns and high explosives were terrible weapons but familiar ones. He knew something about them.

Fighting was a series of such small dangers, limited, instantaneous, each complete in itself, with no continuing or overhanging peril. Moreover, his own tremors were eased by the assurance that his loved ones were not in the same danger that he risked. His home was secure. He had something to go back to.

In other words, the element of safety in all wars previous to the great war closed in November 1918, safety not only of combatant forces relatively, but of civilian populations actually, was large enough to reinforce the self-interest which prompted him to go to war in the first place. Always that self-interest, that determination to get by force what he had been unable to win in peaceful competition, overcame the constantly growing suggestion that war was a foolish, stupid business, entirely unworthy of his experience and his intelligence. He got hard knocks for several thousand years but these scarcely jarred his imagination.

All this time he had been fighting with understandable weapons, hurting his enemies with these familiar weapons or getting hurt by them. There was nothing mysterious about it, nothing to daunt his imagination, stun all thought, fill the soul with dread or unthinkable disaster.

New Machines of War

As rapidly as his enemies found a new weapon he matched the invention with a similar one of his own or a better one. David's sling was the answer to the challenge of the club of the giant of Gath. The blunderbuss was the answer to the cross-bow, even as the arbalest had overmatched the challenge of the longbow. As time went on the long-barreled rifle answered the blunderbuss, the highpower magazine rifle answered the muzzle loader, and the machine gun took up the challenge of the magazine rifle.

Cannon that carry a high explosive shell seventy-five miles replied to the crude ordnance that was the last word in the gunnery of the Spanish-American war. Nitroglycerin and TNT displaced gunpowder. The superdreadnaught of steel crowded from the sea the wooden frigate. Steadily warfare became more perilous, more unendurable, more impressive to imagination, but until the past few years, whatever its killing improvements, the sight and use of man-killing tools did not inspire us with horror.

Old-fashioned war weapons could be felt and seen and heard. They did not drop death upon us from four miles overhead or steal upon us to rob us of life while we slept. They did not freight the wind with danger. When they struck us or burst near us, that was the end of the blow or of the explosion. They did not turn corners to search us out with lung-searing poison or sink treacherously into holes and bide their time for days and weeks to set fire to our lungs or blind us. They were not invisible, inaudible. They were of the known world, changed a good deal from what our greatgrandfathers and their great-grandfathers knew, but still recognizable as the traditional tools of war.

The Creative Chemist's Task

Then the creative chemist, taking a big step forward and making more intelligent use of atomic force, introduced into warfare weapons that could not be seen or heard, that impressed ordinary imagination as things not of this earth at all but of the pit itself.

He showed armies how to use poison gas to kill each other and more often to blind or burn or stupefy each other. He introduced poison into the winds of the heavens and cunningly employed the winds to sweep destruction across wide areas. This new method of making war was the biggest jar ever suffered by our tradition-clinging minds. It was a method which struck at the mind in assaulting the body. Terror unfathomable was locked in it.

Inheritors of subconscious fears two hundred centuries old, curious weaknesses of the spirit that two hundred centuries have not been able altogether to eradicate. Fear of the dark, fear of the unknown, man stood appalled by this new weapon which worked frightful casualties without betraying itself by form or shape or color, without making a sound personal to itself.

It made him think of the future when the inept, unhappy gas contrivances would be so perfected, simplified, concentrated and increased in number and in destructive power, as to make the gas weapons of the Great War as clumsy by comparison as were the smooth-bore rifles of the Revolutionary War compared with the latest Thompson gun.

These things hit at the heart of imagination, surveying what creative chemistry has already done in war in its first few experimental steps. We stand back impressed as never before in the whole history of war tools. We are bound by sheer intelligence to comprehend that chemical science "has only begun to fight." It has learned how to utilize, not very skilfully, a few gases. It has not done anything beyond small-scale experimenting with radioactive forces. But the lessons of the Great War were a tremendous impulse to the research chemist.

The creative chemist is searching out among rare elements, such as radium, arguments against warfare that can no more be refuted than pigmy man can oppose the tornado or the earthquake or contend with Vesuvius. The strange stuff that illuminates the dials of our watches may be the very medium that will eventually produce the resistless force that will make fighting intolerable

Chemists are seeking through forces as yet imperfectly comprehended to turn man toward sanity. They are aiming at his imagination. Who will dare say they are pursuing a fruitless quest after the experience of the Great War which began as a war of great steel projectiles and ended as a war of invisible energy!

Hard-headed military men, usually slow toc onvince that weapons other than the traditional arms of their service must be learned and relied upon, join nowadays with chemists in an appeal to the public understanding which is little short of the striking appeal made by the imaginative story of Mr. Wells, for they realize that chemistry is merely on the brink of great things, and none see so clearly as they that chemistry aims to abolish war by making it desperately perilous to great nations as well as small; to governments as well as to the led peoples; to vainglorious politicians as well as to the obedient servants in uniform.

Wars of the Future

Gentlemen, I have tried to tell you that I believe that the Perkin discoveries of 1856 and their profane application in the hands of the Germans precipitated the trend of events which spelled our late great disaster, and the disaster will recur again in some other form, unless we learn and preach the great lesson to be learned therefrom.

There is one incident which to my mind illustrates every phase of the disconnected thought which I have so poorly expressed to you. In 1906, Sir William Henry Perkin, after England had knighted him for the discovery, the application of which she had so sadly neglected and out of which her enemy was even then forging the weapons of her attempted destruction, came to this country to be present at our celebration of the fiftieth anniversary of his discovery. Medals, banquets, and honorary degrees were presented to him, and in response he said:

> You have been so good to honor me by having this jubilee in remembrance of the part I have taken in connection with this coal-tar industry, and while I am thankful that I had to do with its foundation and early development, yet I feel that the part I have taken is indeed small when compared with the labors of the army of scientific men and others, both inside and outside the color works, who have advanced it to the present condition.
>
> However, it is very gratifying to me to receive all the general and kindly expressions of feeling you are manifesting, and I thank you very heartily. But, what have I that I have not received? It is not, therefore, for me to boast. I can only say in reference to the successes that have attended my efforts: "Not unto me, O Lord, not unto me, but unto Thy great name be all the praise."

On that occasion—the shame of it as we look back on it now—the representative of the development of America's grasp of this discovery who addressed Dr. Perkin and presented the testimonials which brought forth the answer I have quoted, was Dr. Hugo Schweitzer, a chemist, scientist and researcher, a German spy, secret service number 963,192,637, head of the German Secret Service in America, head of the system by which every effort to develop the organic chemical industry in this country was crushed out, head of the system of dye salesmen by which every fact and circumstance of the four million dollars a year American dependent industries was reported to Berlin, carded and charted there, taken into the great industrial establishment at Grosser Lichterfeld, outside of Berlin, and there placed at the disposal of competing German industry; the inventor of the idea of the purchase of the New York *Evening Mail* to corrupt our information; the inventor of the idea of the German Publication Society, formed to publish, for our delectation, the literature of German Kultur; head of the Chemical Exchange, by which all available phenol supply in America was turned away or made inaccessible to the Allies.

Dr. Albert, in praising him, said:

> The breadth of highmindedness with which you at that time (meaning the beginning of the war) immediately entered into the plan, has borne fruit as follows: One and a half million pounds of carbolic acid have been kept from the Allies. Out of this one and a half million pounds of carbolic acid, four and one-half million pounds of picric acid can be produced.
>
> This tremendous quantity of explosive stuffs has been withheld from the Allies by your contract. In order to give one an idea of this enormous quantity, the following figures are of interest: Four million five hundred thousand pounds equals two thousand two hundred and fifty tons of explosives. A railroad freight car is loaded with twenty tons of explosives, the two thousand two hundred and fifty tons would, therefore, fill one hundred and twelve railway cars. A freight train with explosives consists chiefly of forty freight cars, so that the four million five hundred thousand pounds of explosives would fill three railroad trains with forty cars each.
>
> Now one should picture to himself what a military coup would be accomplished by an army leader if he should succeed in destroying three railroad trains of forty cars, containing four and a half million pounds of explosives. Of still greater and more beneficial effect is the support which you have afforded to the purchase of bromine. We have a well-founded hope that we shall be in a position to buy up the total production of the country.
>
> Bromine, together with chloral, is used in making nitric gases, which are of such great importance in trench warfare. Without bromine these nitric gases are of slight effect; in connection with bromine, they are of terrible effect. Bromine is produced only in the United States and Germany.
>
> This in the neutral country of the United States might well

have cost the war and civilization. Thank God, Perkin died before he could see what civilization had done with his discovery.

Gentlemen, personal responsibility is a thing that cannot be escaped. Thinking so we may go to our graves, but there will come forth from the unforeseeable transmutations of destiny or from the Divine will, some reaction of our unconsidered acts or of our deliberate evasion of the moral law that may cause misery to a multitude.

Two years ago there leaned against a lamp-post on the Bowery a stranger, with only his landlady's borrowed quarter in his pocket, only hate in his heart and wrong thinking in his head. To-day, this man, Trotzky, controls the destinies and happiness of three hundred millions of Russian men, women and children. He, the mouthpiece of false ideals, seized upon the ignorant and desperate masses in the hour of their agony. and has proved their destruction.

Contrast his unwholesome and blasphemous career with that of Joan of Arc, who has always seemed so human, so natural, so close to all of us. Her sweet, simple, girlish figure, sublime in her faith, sustained in her virtue and mighty in the power of her dominant will and the justice of her cause. She has been with us now for hundreds of years, and never more so than during this war when she staunched the heart of France and led her brave as of old. As it is with these two individuals of humble origin, so it is with the richest.

Contrast the Emperor of Germany, in whom self-love and ambition had crushed out all spirituality, leading his people and forcing them on in the conquest which has brought such unspeakable misery and suffering to untold millions of men, women and children. Contrast him, I say, with that magnificent figure, Cardinal Mercier, that soul of resistance to injustice and falsehood, whose memory constitutes a solace, stored up for the distressed people of all future times.

As it is with the lowly peasant man or woman, as it is with the emperor on his throne, or a prince of the church, so it is with the scientist or the researcher. Contrast the influences intended by Perkin, who at the end of his life received his richly earned honors with bowed head and in humble voice, "What have I that I have not received? Not unto me, O Lord, not unto me, but unto Thy great name be all the praise."

A New Day Coming

Contrast him, I say, with Schweitzer, the scientist and researcher, representative of the profane application of his science in peace and war, and in the shadow of that contrast, and in the humility and in the shame which we should feel, let us look forward to the day when the English and American chemists can meet again, with the evidence about us of our atonement for our neglect, evidence of permanent peace in all the world, of a higher and more equal standard of living for all our peoples and of a great marching forward in our battle against disease. Until that day, let no man write his epitaph.

Mr. Garvan's address was frequently interrupted by prolonged applause. His audience was fully alive to the truth and importance of the statements made in the characteristic vigorous and fearless manner of the speaker. Here was a man not a chemist, who had made a study of the chemical industry in America and of foreign influence upon it, as it was before the war and as it is now, and he was hitting straight from the shoulder with the evident purpose of awakening every individual chemist to the dangers that lie ahead and to the need of constant vigilance and a renewed pledge that "America First" shall remain the slogan of our chemical industries.

Following Mr. Garvan's address, the following telegram from President Harding to President Smith was read:

The White House, Sept. 3, 1921

President Edgar F. Smith,
American Chemical Society.

It is a pleasure to extend greetings to the gathering of American, Canadian and British societies representing the chemical sciences and industries meeting on American soil. Probably none of the materialistic sciences holds promise of so great contributions to human welfare in the coming generation as that which your organization represents. The developments of applied chemistry involve both a possibility of vastly increased horrors in human conflict, and ultimately inestimable benefits to a peaceful civilization. Let us hope that a science so fraught with either good or vicious possibilities may be turned, through the wisdom of the nations, to the benefit and advancement of mankind.

Warren G. Harding

Secretary Parsons presented the names of Sir William J. Pope, K.B.E., F.R.S., president of the Society of Chemical Industry of Great Britain, and Dr. Paul Kestner, president of the Société de Chimie Industrielle of France, for election to honorary membership in the American Chemical Society. These distinguished foreign chemists had been recommended for this honor by a unanimous vote at the Council meeting on the preceding day. They were elected by a unanimous rising vote of the assemblage of American chemists.

Sir William J. Pope was introduced to the audience by President Smith. He conveyed M. Kestner's regrets that unavoidable conditions had prevented his expected attendance at the meeting and thanked the members for the honors that had been conferred upon them.

Dr. Smith also introduced Professor R. F. Ruttan of McGill University, Canada, and Prof. Ernst Cohen of the University of Utrecht, Holland, each of whom made brief remarks of appreciation of the welcome that had been extended to him.

Secretary Parsons announced that in accordance with action by the Council on the previous day the following resolutions asking Congress to pass a limited selective embargo on synthetic chemicals had been prepared for presentation to the Society:

Believing in the incalculable peace-time benefits which accrue from the development of the science of organic chemistry and its application in medicine, agriculture and the industries connected with foods, fuels, textiles and dyes;

Realizing the great role that organic chemistry has played in the development of chemical warfare, we call the attention of this nation to the grave crisis which threatens our organic chemical industry.

In spite of the tremendous strides made during the past five years in the United States, this important industry is still centered in Germany. Other nations have already sought to safeguard its future in their countries by appropriate legislation. America stands hesitant. Progress has been checked and indeed the very industry is threatened with destruction. Two agencies will be determinative in averting this disaster: the approaching International Conference on Disarmament and the Congress of the United States.

Resolved, therefore,

First, that we urge upon the American delegates to the Disarmament Conference most serious consideration of the broad question of chemical armament as affected by the development and maintenance of the chemical industries in the several nations.

Second, that we urge upon Congress the necessity of including in the permanent tariff bill a selective embargo for a limited period against importation of synthetic organic chemicals, and we express the confident hope that, in view of the important bearing of such action on economic development and on national defense, our representatives, regardless of political affiliations, will support this legislation.

Before putting the motion that these resolutions be adopted, Dr. Smith spoke in part as follows:

My life has been spent in the teaching of chemistry. I know nothing practically of its industrial applications, but having had over fifty thousand students pass through my hands in the course of forty-five years, I met many who gave their lives to our science. They went forth from the halls of the University enthusiastic, hopeful, eager to build up industries throughout the States. One, possessed of considerable of this world's goods, undertook to establish a nitrobenzene industry in the United States. He had training not only in this country but in another country where benzene and its products are common. The result of his experiment was this, that he virtually became a pauper. He lost all that he put into his plant, and of course, his enthusiasm was very much dampened; his ardor was gone.

Again, I was a witness years ago of an effort on the part of educated chemists of the eastern part of Pennsylvania to have glass works in the state of New Jersey undertake the manufacture of beakers, distilling bulbs, flasks and so forth, and they gave us a product that was superior to anything that had come across the seas, but after three years they told us they could not continue. Their competitors got away under them in price, and so that was closed up.

In other words, these native-born, enthusiastic, American chemists felt that their Government had not supported them, and it was quite natural that very few of the chemists of our country were willing to undertake similar projects.

The late war opened the eyes of the world to the fact that God had not given all the gray matter to the people of one nation, but that there were actually chemists on this side of the Atlantic who could do what chemists in another part of the world did, just as well and better. So industries sprang up and there was a revival of that spirit of trying to put our country away out in the forefront, and youngsters seeking an education in chemistry took part. The classes in the universities and colleges were crowded with young men who hoped to become chemists, who hoped to utilize their knowledge in building up the industries of the United States of America.

And then a cold blast came. We all feel it. You and I who are not in the dye industry, you and I who are not connected in any way whatsoever with the industrial work of the country, feel it; sister-professions feel it. And yet there are those who hesitate at this moment to say to our Government, "You must support this dyestuff industry." There are some who seem to be jealous of the dyestuff people. It is not a dyestuff matter; it is a matter that concerns every one of us who is a chemist. We won't have a profession if these efforts which have been put forth in the last five or six years are crushed to earth; it will amount to nothing.

The chemist has not been what you might call a highly respected member of the community. You know that. For years we have gone along the street, and when we told people we were chemists they looked at us askance. What sort of cranks are you folks, anyhow? But we have reached a high plane, and we want to stay there. Our country wants to stay there. Is there an American-born chemist who is willing that his country should be taken down from that high plane to which it has been elevated in these recent years? I am sure there is not.

It is not sufficient for us chemists to touch up our Congressmen and our United States Senators. We have to get close to the people. We have to tell our neighbors what chemistry has done for us, done for them, because the whole matter touches every man, woman and child in the United States of America.

Now, if you approve of these sentiments, and if you will here pledge yourselves anew to work, not only for your science, but for your country, I ask you to adopt these resolutions.

The resolutions were carried unanimously by a rising vote. President Smith now called upon Sir William J. Pope, whose address is printed in full herewith:

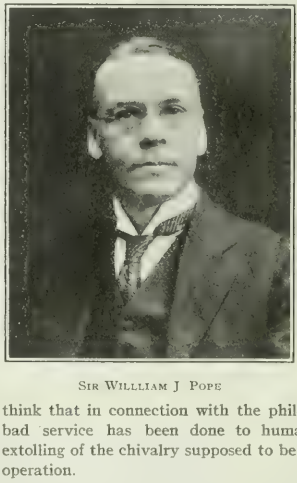
Modern Developments in War Making

By Sir William J. Pope

Every scientific man is becoming more and more convinced that war, if it cannot be abolished, must at least be reduced to a minimum. Every scientific man has become more and more convinced, during the last seven years, that the future of war depends upon science; and practically every scientific man, at least in Great Britain and France, has had seven years cut out of his life and out of his activities in research work by the events of the last seven or eight years.

THE PHILOSOPHY OF WAR

Seeing that we are in a very strong position in this matter, seeing that the future operations of war depend largely upon us, we have a right to complain that the philosophy of war has been very badly handled in the past. We are, in the first place, accustomed to suppose that war exists only during a state of hostility. We are accustomed also to associate with war a certain feeling of what is called chivalry. The idea associated with chivalry has been handed down to us for centuries, principally by poets, by literary men, who have extolled war as a virtuous occupation in that it gives scope to the chivalrous instincts of mankind. My own belief is that war always has been, as it is now, a very dirty business. It is perfectly true that occasions arise during hostilities for the perpetration of noble acts, but those are connected not with war but with one of the few virtues of humanity. A modern battlefield is certainly one of the foulest places that one can imagine, and I think that in connection with the philosophy of war a very bad service has been done to humanity by the universal extolling of the chivalry supposed to be associated with warlike operation.


SIR WILLIAM J POPE

Secondly, the conservatism with which the actual operations of war are regarded largely by military men has again been a stimulus to actual war. During the war from which we have so recently emerged, at any rate during its early periods, I was repeatedly told by military men of very high standing that the war was going to be fought out on the same lines and by the same methods as were used during the Boer war, and the fact that our military men took that view at the commencement of this last great conflict had the effect, I have no doubt, of immensely prolonging the struggle and of very greatly embittering it.

The military mind always resents anything that is new. That has been the case throughout the whole of history. The opposition to novelty in military methods became accentuated as soon as Christianity became a great political power, and during the middle ages there were numbers of instances in which the Vatican issued bulls of excommunication against people who introduced novelties in military weapons. Such a bull was issued, for example, against those who used the arbalest, the machine for throwing big stones, against Christian troops, and history has always been the same.

Furthermore, it is customary to suppose that war exists only during a period of hostilities. That has certainly not been the case during the recent conflict. The war from which we have just emerged did not start seven years ago; it started forty years ago, and throughout that whole period you in America and we in England have been fighting for the enemy. Every dollar which you spent here on German dyes, every pound which we spent in England upon German dyes, was a contribution towards the military war effort, and although we may have done this in the past in ignorance, I venture to think it will be criminal if you citizens of the United States and we British in the future buy German dyes which can be made equally as well here and in England as in Germany, and so contribute to the German war chest. In the same way every dollar which you spend on American-made dyes and every pound which we in England spend on British-made dyes is so much contributed to the defense of our respective countries against a militarism which is still as alive, still as truculent, and still as rapacious as ever.

The Types of Military Arms

I should like to point out in connection with the philosophy of war that a great deal of misunderstanding exists as to the part played by the various types of military arms.

The recent war has seen certain innovations in actual weapons. The aeroplane appeared for the first time. Chemical warfare made its first appearance, and another arm which in my opinion was far more destructive, which contributed far more towards the slaughter and general desolation, also made its appearance for the first time as a serious weapon. That is the arm of preventive medicine.

It is a little difficult for the casual observer to understand why the different types of arms which have been used during the recent conflict have been appreciated in such a variety of ways. When the aeroplane first came in it was received practically with applause. Chemical warfare received universal execration. Preventive medicine was regarded as a very benevolent contribution of science towards the amelioration of the general suffering.

I have a notion that this divergence in opinion arises from the old view that war is a chivalrous pursuit; that it is in the end the highest form of sport. The aeroplane contributes to excitement. Everything which can be introduced in the sport which increases the hazards, which gives the quarry the power of hitting back and perhaps indeed of killing the sportsman, is welcomed. It ministers to the general craving for excitement, and for that reason aeroplane warfare was welcomed as a very fine thing.

Chemical warfare was condemned, condemned in the same sort of way as we in England condemn men who shoot foxes or net salmon. Chemical warfare destroys the sport for the legitimate sportsman. On the other hand, preventive medicine, which was universally acclaimed, is a great thing because it acts as a kind of super-official game keeper. It preserves the game and so provides more material for the legitimate operations of the real sportsman.

The Case for Chemical Warfare

I have no brief for chemical warfare. At the same time, I cannot see that chemical warfare is any worse than any of the other military arms, either high explosives, heavy ordnance, aeroplane bombs, or preventive medicine. There is to my mind only one reason why chemical warfare should not have been introduced. It was introduced by our adversaries, and the reason why it should not have been introduced is that they had solemnly promised on the faith of the Hague Convention not to use it. Apart from this, however, there can be no doubt, I think, that chemical warfare, that chemical arms constitute a very humane weapon of war.

Public opinion on this subject is grotesquely ill-informed, at any rate in England. I am not acquainted with the way in which public opinion regards chemical warfare in the States, but in Great Britain, the views, the sort of philosophy put before the general public in connection with chemical warfare, is ridiculous. I can illustrate this very well indeed by quoting from a very weighty letter which appeared in the *London Times*, our first British newspaper. This letter was signed by eight of the most eminent medical men in Great Britain, the eight men who stand in the highest official positions in crown offices connected with medicine and surgery in Great Britain. The letter urges that the Committee of Nations should prohibit chemical warfare and states that the use of gas is self-condemned for the following reasons: "It is an uncontrollable weapon whose effects cannot be limited to combatants. It is an unclean weapon, condemning its victims to death by long-drawn-out torture. It opens the door to infinite possibilities of causing suffering and death, for its future development may well lead to the devising of an agent which will blot out towns and even nations."

If you will keep that quotation in your minds and allow me to call attention to two or three facts connected with poison gas and chemical warfare generally, I think you will see that the letter states a position of a hopelessly impossible kind.

The fact is that poison gas is far less fatal and far less cruel than any other instrument of war. One of the greatest discoveries made by the Germans during the war was that mustard gas is a more efficient agent than any other previously employed for causing casualties. The introduction of this material led to an appalling lengthening of the casualty lists, and the fact that the French, the Americans, and the British had in sight an overwhelming production of mustard gas was certainly one of the great factors in deciding our adversaries to ask for an armistice.

Among the total mustard gas casualties, death occurred in about two per cent of the cases, and when death did not ensue, complete recovery resulted in almost every case. In two or three per cent of the casualties, the victim was left with some permanent disability; in general, however, not of a very important kind.

It is quite unnecessary to dwell upon this very merciful result, and to contrast it with the proportion of deaths among the casualties from high explosive shells, from bayonet wounds, from projectiles, and with the number of maimed, crippled, and shell-shocked that we see around us every day.

Other materials of chemical warfare which were in use at the armistice did not kill at all; they led to certain lesions, which in the great majority of cases were discharged permanently cured after about six weeks at most in hospital.

The letter implies that the ordinary weapons of war do not affect noncombatants, that the unclean weapon is the only one which condemns its victims to death by long-drawn-out torture, and asks that chemical warfare should be abolished on the ground that, unlike other weapons of war, it is capable of being improved. Everyone who has watched the casualties passing from the front to the dressing stations recognizes that projectile wounds are far more ghastly than the lesions caused by poison gas. Those who have seen Verdun and Ypres know what high explosives have already done towards the blotting out of towns.

But in order to focus attention upon the argument which I am now trying to develop, I should note that although accurate data are not at the moment available, the gas casualties, the casualties due to the employment of chemical agents in the recent war, numbered several hundred thousand only.

Preventive Medicine

Let us turn from chemical warfare, with its comparatively small casualty-producing power, to the arm of preventive medicine.

Every great soldier has realized that an army is limited in size by the difficulty of keeping it free from disease and epidemic in the field. This fact, for ages past, has kept the maximum size of an army down to something of the order of one hundred thousand men. When the resources of preventive medicine were enlisted and properly applied, the unit dimension for an army became a million men. Preventive medicine made it possible to maintain twenty million men under arms and abnormally free from disease, and so provided greater scope for the killing activities of the other powers.

A very competent observer gives fifteen millions as the number of combatants who were killed during hostilities in the recent war. Nine-tenths of this achievement is attributable to preventive medicine. Further, the keeping of these vast armies in the field led to the disorganization of all civilian activities and to the dissemination, consequently, of epidemic disease to noncombatants. A great part of this death roll—a death roll amounting possibly to twenty millions, a death roll which is still being added to—is to be attributed to the operations of this most powerful of the newer military arms.

I merely quote this to show that our philosophy of war has been founded upon an entirely wrong basis up to the present, and that we must enlarge to a very considerable extent our conception of what takes part in military operations. We have not only the actual operations of the soldier himself, but the operations of the medical men who are generally supposed to be purely beneficial agents in connection with the conduct of hostilities, and in diminishing the death rate. It is, to my mind, perfectly clear that the very eminent signatories of that very powerful letter in the *London Times* were giving vent to a philosophy which was entirely unsound and entirely irrational.

In the end, when we consider this whole question fully, it is impossible for us to lay the responsibility of warlike operations merely upon the soldier. We are all of us responsible. The chemist has been largely responsible, the medical man has been responsible; the man who bought the German dyes has been responsible, and the man who contributes to war funds; we are all of us in the same boat, and I hope that, so far as your country and mine are concerned, we shall long remain in the same boat, and that we shall long persist in doing everything that we can to prevent the recurrence of such times as we have passed through during the last seven or eight years.

Professor R. F. Ruttan delivered an address on the organization of industrial research in Canada. This contribution is printed below:

A Plan for the Development of Industrial Research in Canada

By R. F. Ruttan

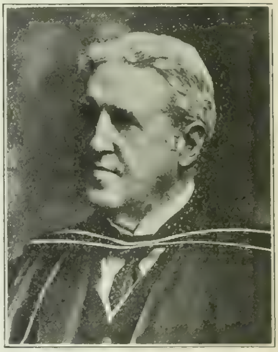
In 1916 the government of Canada by order-in-Council established an Advisory Council for Scientific and Industrial Research. This corresponds very closely in organization to the National Research Council of the United States, and was modeled largely on the Advisory Council for Scientific and Industrial Research in Great Britain which has now become the Department of Scientific and Industrial Research of the British government.

Among the duties assigned to us as a Council, we were required to ascertain and tabulate the various agencies conducting research in the universities and in the industries, but especially to make ourselves, to quote from the government mandatè, "acquainted with the problems of a technical and scientific nature that are met with by our productive and industrial interests, and to bring them into contact with the proper research agencies for solving these problems, and thus link up the resources of science with the labor and capital employed in production so as to bring about the best possible economic results."

As a result of a careful survey of the research carried on in Canada and of the scientific organization the industries, we were reluctantly compelled to recognize the fact that scientific research in Canada was practically confined to the laboratories of two or three of our universities and one or two departments of the government. So far from there being any research in the industries, we found the absence of any scientific control to be the rule rather than the exception. The industries were in the rough, pioneer stage of organization.

Promotion of Research by the Council

By means of lectures, bulletins and addresses before the Canadian Clubs and Boards of Trade throughout the Dominion, and frequent conferences with the branches of the Manufacturers' Association, we successfully directed attention to the value of scientific method and research. A demand for university trained men in the industries resulted. The Council began at once to aid in training men for research by establishing a system of studentships and fellowships to encourage graduates of special ability to enter the field of research, thus providing trained minds for fundamental and technical research. This year we are sending about fifty of the best graduates of our universities into scientific research work in graduate schools.


R F Ruttan

We gave substantial financial assistance to researches, both academic and industrial, on the whole with very satisfactory results. During the summer of 1917 we cast about to find some comprehensive and effective system by which scientific and industrial research in Canada could be developed. We naturally studied the plans for promoting industrial research under consideration or actually in progress in Great Britain, and in the other dominions of the Empire, as well as in France and Italy. We were kept informed by correspondence with the National Research Council of the United States regarding their plans and organization. We were in the fortunate position of having a clean sheet on which to make our plans. Canada had no national research institute, no bureau of standards, no national physical laboratory, no privately endowed institutes for research.

The technical and scientific laboratories of the various departments of the Federal government were isolated units, each intent on its special work, doing it well but with no coördination or coöperation and not in intimate relations with the industries of the country. The universities were similarly isolated from the industries and, with one or two exceptions, teaching and administration work absorbed all the energies of the staff and all the available resources. Training in research was confined to two or three of our large universities.

The difficult task of bridging the gap which separates science from its applications to industries is one which has in recent years called for the closest consideration of the leaders in science in every country. This problem, so vital to the nation, had to be solved by us in a way to give the best results under the conditions as we found them in Canada. We recognized that the liaison between science and its applications could be effected only by organized effort, by bringing about an intimate coöperation between those who could set the industrial problems and those whose training and knowledge would aid in their solution.

ESTABLISHMENT OF CENTRAL RESEARCH INSTITUTE

We finally decided in 1917 upon the policy of establishing a Central Research Institute for both scientific and industrial research. This general plan for developing research in Canada met with the cordial approval and encouragement of the National Research Council, and the group of representative scientists in Washington during the winter of 1917 to 1918. We had the advantage of several conferences at Washington with many of the leaders of scientific organization in this country by invitation of Dr. Hale, then president of the National Research Council

As finally developed and outlined in Bill 116 of this year's parliament, the National Canadian Research Institute was practically unanimously approved by the Cabinet and passed the House of Commons without division, but, owing to an unexpected attack of economy on the part of the Senate, the Bill was not confirmed but postponed until next session. Notwithstanding the vote of the Senate, the Cabinet gave us a special grant of $100,000 which will enable us this year to make a small beginning by securing a site and preparing detailed plans of the buildings. The first building will be a four-story unit, 200 by 60, with a well designed power plant attached, capable of extension and adjustment. It will be erected on a site near Ottawa, sufficiently large to give ample room for expansion, with a flexible organization to enable its activities to be adapted to the varying requirements of a rapidly growing country like Canada.

ACTIVITIES OF THE INSTITUTE

The activities of the Institute may be classified briefly as follows:

1—It will be the Bureau of Standards for Canada and will have charge of the standardization and certification of the scientific and technical apparatus and instruments for the government service and for use in the industries and laboratories of Canada; and the determination of the standards of quality of the materials used in the construction of public works and of the supplies used in the various branches of the public service. As applied to the industries, it will investigate methods of standardization and measurement generally, the physical and mechanical properties of such materials as are used by a large number of industries. The unification of standards will be carried on in association with the Committee on Engineering Standards now doing excellent work in Canada.

2—Closely associated with its function as a Bureau of Standards, it will carry on fundamental research in chemistry, biology, physics and related fields, investigations similar to those engaging the attention of university professors in scientific laboratories.

3—Investigations in biochemistry and bacteriology, both general and as applied to such industries as the fisheries and packing industry.

4—Investigations undertaken on recommendation of the Research Council from time to time to promote the utilization of the natural resources and valuable waste materials of the country.

ORGANIZATION OF THE INSTITUTE

The type of research work described under these four heads will be carried on by the permanent staff of the Institute, associated with specialists engaged from time to time. The heads of departments will be chemists, physicists, engineers, and other scientists who have already shown high capacity for investigation and will be allowed the greatest possible opportunity to carry on fundamental research, each along his own line. We do not intend to lose sight of the significance of the individual in research. Coöperation in investigations of national importance requiring the combined efforts of chemists, physicists, and engineers will be planned by the director in council with the heads of departments, when such problems meet with the approval of the Research Council and the director.

This group of twelve or fifteen highly qualified investigators will form an advisory body for the industrial specialists who will be engaged by the Research Council or paid by the industries "to conduct investigation and standardization at the request of any group of industries in Canada concerning the materials used by them or of the products of such industries."

They will, from time to time, assist in and act as consultants in researches undertaken with the object of improving the technical processes and methods used in the industries of Canada, and of discovering new processes and methods which may promote the expansion of existing, or the development of new industries.

The director, in consultation with the Research Council or a committee of the Council, has the power of deciding on the technical processes and methods which require and would justify investigation and the conditions under which they should be undertaken.

We are establishing in Canada a number of associations for research in the industries, similar to those in England and the United States. These trade guilds for research, as we call them, will pay their own specialists, the Institute providing the laboratory accommodation and facilities available in its building without rental. A nominal charge only will be made for power and materials. Several are now being organized.

Under conditions to be determined in each case, laboratories will be placed at the disposal of individual industrial firms, for study of improvements in processes and utilization of by-products. The length of time these laboratories may be occupied and the conditions of secrecy regarding the work will be similar to the requirements of the Mellon Institute. In this phase of its activities, the Research Institute will parallel the Mellon Institute, with this difference, that instead of being maintained by private endowment it will be endowed by the government of the country.

The difficulties in equipping and manning any institute capable of carrying on more than a fraction of the manifold industries of the United States or of Great Britain are almost insuperable. This, we have concluded, is not the case in Canada.

A central research institute, having functions such as described, is applicable to a country like Canada having comparatively few very large industries and a number of unimportant ones scattered over many thousands of miles. Many of these industries are quite isolated from sources of information and materials for research.

The bill passed by the Cabinet and House of Commons of Canada further provides that, when instructed to do so by the Governor in Council, the Institute should assume a part or all of the research work now carried on in the various departments of the government, or, when found desirable for the sake of efficiency or economy, these investigations should be coördinated and supervised by the Institute, under conditions approved by the Research Council

PATENTABLE DISCOVERIES

The difficult question of remuneration for valuable and patentable discoveries has been left largely to the discretion of the Research Council. Article 16. dealing with this subject which is of general interest, reads as follows:

> All discoveries, inventions and improvements in processes, apparatus or machines, made by a member or any number of members of the technical staff of the Institute, shall be vested in the Council and shall be made available to the public under such conditions and payment of fees or royalties or otherwise as the Council may determine, subject to the approval of the Governor in Council. The Council may pay to technical officers of the Institute and to others working under its auspices, who have made valuable discoveries, inventions or improvements in processes, apparatus or machines, such bonuses or royalties as in its opinion may be warranted.

The intention of the Council is to give a liberal share in the commercial rights of all such discoveries. Its function is to develop research, not to exploit it.

To illustrate this policy, all discoveries of commercial value made by persons receiving grants of money from the Council to meet the expense of researches, many of which have industrial applications, are practically the property of the investigator. The discoverer is given the right to patent his results, and, except where the discovery is of national importance, he reaps the whole benefit of his research. The extent to which he will participate, if he is not given the entire proceeds of his patent, depends largely on the part played by the grant in bringing about a successful result. In the case of inventions and discoveries made by technologists in the employ of the government or by holders of fellowships, etc., whose whole time is paid for by the government or the Council, the conditions are different; the practice in these cases has hitherto been to allow a half interest in each patent taken out for Canada, the remainder being retained by the government or Council and applied to the advancement of research. The discoverer has been, however, allowed to patent his results in other countries than Canada and to receive the whole of the royalties, etc., resulting.

The staff of the Institute will consist of a director and a group of scientific and technical officers appointed by the Research Council, which latter body shall prescribe their remuneration and tenure of office, always subject to the approval of the Governor in Council. The director will be given a very free hand and will receive a salary commensurate with his responsibilities. The act states that he shall control the work of the Institute, report to the Research Council at intervals, shall have a right to be present at and take part in meetings of the Council while matters affecting the work of the Institute may be under consideration.

A good reference library will be provided, the nucleus of which is already in existence. Bulletins and reprints will be regularly issued to keep the general public and the industries in touch with the character and extent of the investigations.

The Institute will not be a department of the government, but one of the activities of the Research Council. The Research Council is, by the act, made a body corporate under the Canadian government, with powers to hold lands, receive donative bequests, etc. The Research Council and the government are equally determined to keep the Institute free from political influence and party patronage, hence the powers given the former to make all scientific and technical appointments and to fix salaries. Only clerks and nontechnical employees are to be appointed through the Civil Service Commission of the government. The responsibility for the success or failure of this venture is placed upon the shoulders of the Research Council and the director in charge.

RESULTS ANTICIPATED FROM THE INSTITUTE

We hope that such an Institute will give us the following results:

1—It will bring into harmonious and profitable contact men interested and skilled in fundamental or academic research and those interested in the applications of science to industry.

2—It will offer a career in Canada to the young graduate who has shown capacity as a scientific scout in some field of science. We realize, to quote H. G. Wells, that "to educate without creating opportunity is to set a bonus upon the export of national ability." It will stimulate and develop the graduate schools in science, and will in turn be a source of supply of men capable of conducting real research for the industries and universities of Canada.

3—It will encourage the organization of industries into guilds for research to enable each industry, as a whole, to meet competition by providing them with free laboratories. Relieved of the expense of building and maintaining a laboratory, a group of kindred industries could well afford to pay a specialist, or a group of researchers, a salary that would attract an efficient man even from Europe. Obviously, industrial research in the Institute cannot be satisfactorily conducted beyond the laboratory or semicommercial stage. The works themselves must deal with the technical research on a commercial scale. While we are most anxious to have the industries take a great part in the work of the Institute, it is not sufficient for Canada to provide only for these guilds for research and individual investigations; industries work for the profit of to-day, the Institute must also look to the preservation of the national wealth of the future.

Underwood and Underwood

SIR WILLIAM J. POPE AND BRIGADIER GENERAL AMOS A. FRIES

4—It appeals to the Research Council especially on the grounds of economy of administration and ease of research control.

It is obvious that there are many cases in which the functions of the Institute outlined above will overlap, which in scientific work is by no means an unmixed evil. Overlap is the bogey of the official mind. The whole plan makes no claim to logical completion; it is rather the beginning of an organization to develop industrial research in Canada, which should in time become more compact and efficient. I think I may claim for it that it is facing in the right direction.

The meeting adjourned upon the conclusion of Prof. Ruttan's address.

....

SYMPOSIUMS AND SPECIAL ORDERS IN DIVISIONAL MEETINGS

A glance at the list of papers in the official program under the various section and division headings will convince anyone of the tremendous growth of chemistry and chemical research in the United States. It will also indicate the increasing tendency toward specialization in the various branches of chemistry. An outgrowth of this specialization is the grouping of papers related to the same phase of one particular chemical specialty. Symposiums are therefore growing in connection with the divisional meetings.

The Division of Biological Chemistry conducted a symposium on vitamines which proved to be of great interest. It was brought out that important strides have been made in the study of these food accessories. Their relation to health and nutrition is receiving attention on the part of biologists and medical scientists, but the chemist is delving into the composition of these complex bodies with the desire to split them into their ultimate constituents and possibly find ways and means of preparing them without the aid of nature. The papers read at this symposium were the subject of most earnest discussion on the part of the active workers in this field, and led to practical results in the appointment of a committee to stimulate further research.

The Division of Industrial and Engineering Chemistry held symposiums on three subjects, filtration, chemistry of gases and fuel, and metric standardization. The first subject was handled by a group of speakers whose experience covered practically every type of filtering process, and the papers presented will appear in the November issue of THIS JOURNAL. The symposium on the chemistry of gases and fuels included a general discussion of chemical problems and chemical achievements in the field of gases, coking, and fuels. It is more fully reported on page 956.

The Committee on the Metric System of the AMERICAN CHEMICAL SOCIETY has become very active in behalf of world standardization on a metric basis, since E. C. Bingham has become its chairman. The conference held in connection with the meeting of the Division of Industrial and Engineering Chemistry was attended by men from the industries, college men, officials from the Bureau of Standards, and others.

Dr. Bingham opened the conference by reading a paper on the "Adoption by the Colleges of Standard Metric Units." (This paper will be published in the November number of THIS JOURNAL.) Dr. Bingham brought out that practically all institutions, from which responses had been received to a request that they order chemicals and other supplies in metric units, had agreed to comply with this request. This has brought about some changes in the attitude of supply houses, most of which now furnish chemicals and other materials both in metric units and in the present trade units.

The ease with which the metric system can be made to fit industrial processes and the advantages of its general, universal application were brought out by various speakers. The discussion was participated in by W. A. Noyes, H. D. Hubbard, W. D. Collins, Charles L. Parsons, and many others. Hearings are shortly to be held on the Bill now before Congress, H. R. 10, providing for the introduction of the metric system as the national system of weights and measures, within ten years of its enactment. The Advisory Committee of the AMERICAN CHEMICAL SOCIETY was requested to consider the advisability of endorsing this measure and reiterating its stand in favor of the adoption of the metric system in the United States.

In the Petroleum Section a group of papers arranged under the subject of emulsification problems aroused interest not only among the oil chemists, but among manufacturers whose plants discharge emulsified oil into tidewaters. The papers brought out some points which it is felt will have important bearing on the solution of this difficult problem of handling wastes containing oil emulsions and will be treated in the November number of THIS JOURNAL.

Close observers of the growth of the AMERICAN CHEMICAL SOCIETY have noted with considerable interest the natural expansion of sections and divisions devoted to specialized subjects. For years teachers of chemistry have been among the most prominent members of the SOCIETY and have contributed largely to its programs, as well as taking an active part in its management. But it was not until the Rochester Meeting last spring that any keen desire was manifested on the part of teachers of chemistry to get together and discuss their problems in a separate section. Dr. Edgar F. Smith, who is naturally interested in matters of education, with the help of a few kindred spirits arranged for a Section of Chemical Education at the New York Meeting and, judged by the attendance at the three sessions held, this Section will soon become an important factor in the work of the SOCIETY. The first meeting, held Wednesday afternoon at 2 P.M., was so well attended that it was necessary to move to larger quarters for the two remaining sessions. Indeed, one might have called the roll of the American universities and colleges where chemistry is taught, and found a comprehensive representation. Industrial men likewise showed by their interest that they appreciated the significance of these sessions.

The meetings of the fifteen divisions and sections extended over Wednesday afternoon, Thursday morning, and the entire day on Friday. Full reports of these meetings will be found on pages 956 to 960 of this issue.

……

SOCIAL FEATURES

At 4 P.M. on Wednesday afternoon a reception and lawn party was given by Columbia University on the University Green. This occasion offered one of the few opportunities throughout the busy week for renewing acquaintance with regular attendants at the meetings of the SOCIETY and for meeting newcomers. Band music enlivened the occasion and a buffet luncheon was one of the enjoyable features.

The big get-together feature of the social program for the men was the smoker given in the ballroom of the Waldorf-Astoria Hotel. British and Canadian visitors occupied the boxes. A pleasant evening of fun, smoke, and good cheer was provided. Songs by the audience, as well as by professional artists, several vaudeville numbers, cartoons of prominent members thrown on the screen, and a play entitled "What is a Chemist?" written and staged by Ellwood Hendrick, constituted the program. The play was a clever take-off on the relation of chemists to big business men before and after the slump in business. Mr. Hendrick himself played the leading role.

About 500 members and guests attended the formal banquet in the ballroom of the Waldorf-Astoria on Thursday evening. Dr. John E. Teeple was the toastmaster. Referring to the American, British, and Canadian flags above the speakers' table, he proposed a hearty toast to the President, one to the King, and one to our guests. Among those who later responded in characteristic vein to the toastmaster's call were Sir William Pope, Dr. G. S. Whitby representing Dr. Ruttan, General Fries, Dr. Smith, and Dr. Bancroft.

……

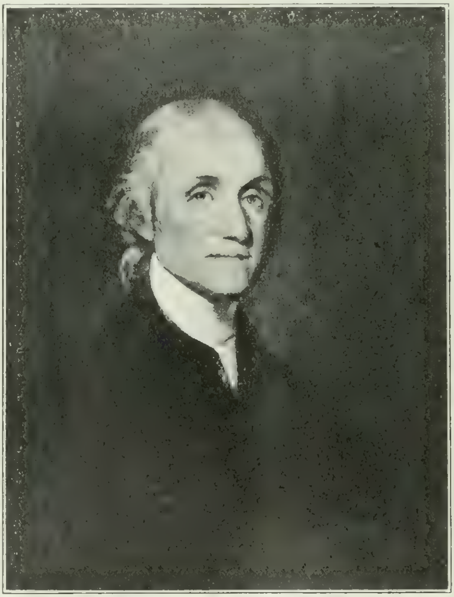
PUBLIC MEETING

A large audience assembled in the Gymnasium of Columbia University, Friday evening, September 9, at 8 P.M., to hear President Smith's lecture on "Progress in Chemistry." At Dr. Smith's request Sir William J. Pope assumed the chair. Sir William first introduced Dr. C. A. Browne, chairman of the SOCIETY's Priestley Memorial Committee, who presented a portrait of Priestley copied from an original Stuart. This portrait is to be hung in the National Museum at Washington, D. C. In making the presentation Dr. Browne delivered the following address:

> It is perhaps fitting on this occasion to say a few words of appreciation about this man whom science has always delighted to honor. We chemists remember him as the discoverer of oxygen, ammonia, hydrogen chloride, sulfur dioxide, nitrous oxide, and various other gases—as the greatest pioneer, so to speak, in that branch of our science known as pneumatic chemistry. Yet Priestley was more than a chemist. If a clergyman were asked, he might say, according to his school of belief, that Joseph Priestley was either a great heretic, or a great teacher of liberal religion. A student of politics might state that Priestley is to be remembered for his part in the great democratic movement which reached its climax in the American and French Revolutions. An inventor might tell you that Priestley's fame rests chiefly upon his invention of soda water, for which he won the

Copley medal. A philanthropist might add that Priestley, from the reforms which he initiated in education and in the laws governing dissenters, was a great humanitarian. Similarly a plant physiologist, an historian of science, a student of letters and a sociologist might each claim Joseph Priestley as his own. Judged by the titles of his one hundred fifty books and pamphlets, Priestley's interests were devoted about fifty per cent to theology, twenty per cent to chemistry, and ten per cent each to philosophy, politics, and education. Theology was his vocation and chemistry only a major avocation. What this versatile genius might have accomplished, had he devoted all his energies to chemistry, is difficult to imagine. Priestley believed the frequent change from one occupation to another to be beneficial, and it is significant that other great men, who have been distinguished for their versatility, have expressed a similar opinion.

But it is for his work in chemistry that we, of this SOCIETY, honor Joseph Priestley, and it will be interesting to measure him with other noted chemists of the past. Some twenty years ago, Prof. Cattell, the editor of SCIENCE, published a list of the thousand most famous men arranged in the order of their eminence, as determined by comparing the average length of their biographical sketches in different American and European encyclopedias. According to this estimate, the most famous chemist is Sir Humphry Davy; then follow in order Gay-Lussac, Faraday, Priestley, Boyle, Liebig, Lavoisier, Berzelius, Paracelsus, and Rumford. This classification, although imperfect and subject to later revision, yet has a significance. Joseph Priestley is fourth upon this list, but if we measure him by his estimation in English-speaking countries alone, he will easily rank first. In the public library of this city there are two hundred index card references of books, tracts and articles about Priestley to fifty or less for each of the other chemists, while in the English "Dictionary of National Biography" there are twenty pages about Priestley to twelve or less about Davy, Faraday, or Boyle. The hold of Priestley upon the thoughts of English-speaking people is tremendous and it is destined to endure as long as the English language is spoken. He is one of those common possessions, which, belonging to England and America alike, work for unity of thought and feeling. Rumford, the founder of the Royal Institution and of the Rumford Professorship at Harvard, is another such common possession. Unjust suspicions and threats of violence forced Rumford to seek refuge in England; religious and political persecutions forced Priestley to find an asylum in America. Although forcibly accomplished, it was our first exchange of scientists. We do things better in these days. What good relationships were cemented between Canada, the United States and England by that eminent scientist, Sir William Osler, at the universities of McGill, Pennsylvania, Johns Hopkins, and Oxford.



PORTRAIT OF JOSEPH PRIESTLEY

Priestley was said by Pattison Muir to be an alchemist and not a chemist. We should qualify this view perhaps by saying that he was the connecting link between the old order and the new. Some of the members of this audience may have seen Liebig, one of the founders of modern chemistry, who was born the year before Priestley died. Priestley, the last defender of phlogiston, was born the year antedating the death of Stahl, the originator of phlogiston. These three lives, Liebig, Priestley and Stahl, carry us back from the present age to the time of Robert Boyle and the alchemists.

Probably no chemist ever had so many tricks played upon him by Dame Fortune as Joseph Priestley. His habit of stammering forced him for a time to abandon the ministry for teaching, and his chance acquaintance, while a teacher, with Benjamin Franklin in 1766, led him to take up experimenting. Franklin, whom Matthew Arnold once called our greatest American, exercised a powerful influence upon Priestley and it is remarkable how much the latter resembled Franklin not only in love for experimental science, but in versatility and in liberality of opinions.

Accident was a determining factor not only in Priestley's life but also in his experimental work. While Aug. 1, 1774, is given as the date of Priestley's discovery of oxygen, he had already prepared this element three years before without knowing it. He isolated chlorine without realizing its importance. Priestley's method of experimenting was like that of an angler who, following a crooked path, throws his line haphazard into every pool and stream. As Sir William Ramsay once remarked, "He fished everywhere and caught many large fish." This random method of angling and adherence to one crooked path caused Priestley, however, to miss catching many fish equally large He had the law of multiple proportions and other important deductions on his hook and let them escape. But many other noted experimenters have lacked the carefully controlled imaginative power which is so necessary for accurate scientific deduction Hofmann once said that he would surrender all his discoveries for the one brilliant idea of Kekulé. Priestley expressed no such vain regrets. He was aware of his limitations as a theorist and was content to be known as an experimenter. "It is not my opinions," he once wrote, "on which I lay stress. Let the new facts, from which I deduce them, be considered as my discoveries and let other persons draw better inferences if they can."

Priestley's mind, to employ a chemical term, was intensely catalytic. He had the faculty of setting men's intellects into a ferment of activity, and this was as true in America as it was in England. Read Prof. Smith's little book, "Priestley in America," and see how constantly he was occupied the last ten years of his life. Everyone came to feel the influence of his personality from Presidents Washington, Adams and Jefferson down to his neighbors in Northumberland. He argued with our clergymen, he debated with our scientists, he disputed with our politicians. Our great lexicographer, Noah Webster, absorbed as he was in his dictionary, laid aside his work to have a brush with Dr. Priestley.

Yet it must not be inferred that Priestley was naturally perverse or quarrelsome. He was exactly the opposite. His simple truth-loving nature made him the perfect expression of amiability.

He paid smiling attention to the arguments of his opponents and so it happened that those who differed most from his opinions were often his strongest friends. The noted hymn-writer, Toplady, although of opposite religious convictions, said this of Priestley, "I love a man whom I can hold up like a piece of crystal and look through." Nothing better can be said, for it explains the secret of Joseph Priestley's greatness.

At a memorial meeting in honor of Leo Tolstoy not long ago, there were shown as part of the exercises moving pictures of the great Russian writer. This Memorial Committee wishes it might show you such moving pictures of Joseph Priestley. Views of the old doctor working in his Northumberland laboratory or planting his garden or playing chess with Mrs. Priestley would be well worth seeing. But the chairman of our Committee, President Smith, with all his love and veneration for Priestley, could not accomplish the impossible. He has, however, out of the one hundred or more paintings, engravings, casts, medallions, and busts which have been made of the famous philosopher, selected the one likeness which Dr. Priestley's family always considered to be the best and has had it reproduced. And this is the picture, a faithful copy of the famous Stuart painting. It is to hang in the National Museum with the portraits of Franklin, Washington, Adams, Jefferson, and the other great men of our country whom Priestley knew and inspired. May we and the future generations of chemists, who look upon this likeness, receive a share of the same inspiring influence.

The task of the president of the SOCIETY in addressing the public meetings held in connection with the semi-annual conventions is difficult. His audience is composed of laymen who are not necessarily grounded in the principles of science, as well as members of the SOCIETY. The president must have a message of interest to both groups and he has a splendid opportunity for further emphasizing the importance of chemistry to all humanity, its historic background, its rapid advancement, and its continued search for new fields of service.

Underwood and Underwood

GROUP AT THE CHEMISTS' CLUB

MRS. KENDALL, DRS. PARSONS, SMITH, JORDAN, NICHOLS, ZANETTI, TEEPLE, MACKENZIE, MOODY, ROSENGARTEN, MRS. HESSE

No one who had the privilege of listening to Dr. Smith's address at the Public Meeting can help but feel that he rose to the occasion beautifully.

His treatment of the progress of chemistry revealed the historian of American chemistry at his best. His loyalty to the science which he has taught thousands of young men, many of whom are leaders in industry and education to-day, and his keen desire for progress in both pure and applied chemistry stand out in the following words which are quoted from the address:

> The burden of my desire is that the youth of the land, entering our science, shall be broadly and fundamentally trained in its principles and in its achievements. That, while they may glory in their own particular successes, mental and material, they shall constantly say to themselves, "What have we done for our country?" until the time comes that they may have the happiness of thinking that they have contributed in some way to the progress and to the good of humanity. They should in all sincerity believe that "Chemistry is most honorably, when she is most usefully employed; and is equally in her own proper element when analyzing the diamond with Davy; and when descending, with humble industry, to the assistance of the manufacturer at his loom, or the dyer over his vat."
>
> My desire would have no East, West, North or South in chemistry, but one united body from all sections, eager to carry the science into every walk of life—even into the halls of government that their occupants may understand how intimately chemistry is interwoven with the laws and welfare of the land.

International Meeting

The Great Hall of the College of the City of New York was filled to capacity when President Smith opened the International Meeting on Thursday, September 8, at 2:30 P.M.

An organ recital by Prof. Samuel A. Baldwin, head of the Department of Music of the College, immediately preceded the meeting and was greatly appreciated by those in attendance. The numbers were well selected and beautifully rendered and the audience did not hesitate in expressing its warm approval of this splendid preliminary feature to a momentous meeting.

After a few words of praise for the spirit which had prompted this gathering of the chemists of English-speaking nations and the efforts which had been expended by the committee on arrangements, President Smith introduced Prof. Charles Baskerville, head of the Department of Chemistry of the College of the City of New York, who welcomed the gathering on behalf of the Trustees and Faculty of the College and delivered the first of the eight addresses on the general theme "Chemistry and Civilization." Dr. Baskerville's address was entitled: "Science and Civilization: The Role of Chemistry." He spoke, in part, as follows:

> An inventory shows that more changes and greater changes have taken place in civilization during the past one hundred and fifty years than in all the preceding centuries of recorded history. It staggers the intellect to contemplate the stupendous list of material facts and scientific conceptions that have become ours in that sesquicentennium. Practically all the chemical elements have become known since 1772; all we know about electricity and communicating with one another through space; ideas of dynamics; the steam and gas engines involving transportation by land, water, and air; ability to see the invisible; X-rays, and the remarkable phenomena of radioactivity; bacteria and immunology and serum therapy; organisms held in suspended animation caused to function again. Many of the miracles of the New Testament are everyday acts of master surgeons to-day. All these things, their correlations, their permutations, their coördinations, adjustments and applications have brought the individual into touch or into communication with all other individuals of our world. Thus science has made human history at overwhelming speed.

The speaker then dwelt at length upon the misuse of scientific achievements for war purposes by our enemies in the World War and referred to the need for recovering from this tendency, in the following words:

> The situation thus is such now that man must solve the dual problem not only of regaining the position of dignity which distinguishes him from animals of a lower order, but of establishing himself upon the plane we think worthy of the noblest development of nature, the study of which we call Science.

He then reviewed the development of the university and the influence which it has wielded since it first became a factor in the onward trend of civilization. He referred also to research and its influence upon the development of science, and continued as follows:

The part played by science in bringing about the conditions obtaining has laid upon itself a serious responsibility to find a way out, else more war, more destitution, continued hatred of class against class, people against people. * * * With all deference to the followers of all the arbitrary divisions of science, it may be positively asserted that life processes and human thought, hence conduct, are intimately related. The life processes depend upon chemical changes, speed of the changes, diffusion of the products, energy involved, its direction, and what-not other factors with many of which we are already familiar through published researches. Their direction will depend entirely upon the factors in the systems and how man controls them.

President Smith then introduced Dr. Arthur D. Little of Boston, who addressed the meeting on "Energy: Its Sources and Future Possibilities."

This subject was handled in Dr. Little's usual masterful manner. He marshalled scientific facts and statistics to bring out the need of finding new sources of energy to replace our rapidly dwindling supplies of coal, oil and natural gas, or devising ways and means of using these supplies with greater economy and efficiency and less waste.

Excerpts from this address follow:

In appraising the sources of energy we must consider form values as well as qualities available. Gasoline can be utilized more effectively than coal. The development of water power involves a heavy initial expenditure, and therefore interest charges are the chief item of expense.

* * * * *

We are cognizant of sources of energy inconceivably greater than any possible requirement of the human race. There is to be considered, first of all, the radiant energy of the sun, of which Lodge assures us the earth receives only one-one-hundred-and-fifty-millionth part. It seems too little to talk about. It is only three small calories per minute per square centimeter of the earth's surface. But Ciamician has calculated that a surface of only 10,000 square kilometers receives in a year, assuming only six hours as the effective day, a quantity of heat that corresponds to that produced by the burning of 3650 million tons of coal. That is considerably more than double the entire world production. The world awaits the genius who will convert radiant energy into electric current. Of that minute portion of the solar energy received by the earth only about one-three-hundredth part is stored up by the plants. They, nevertheless, produce annually, according to Ciamician, thirty-two billion tons of vegetable matter, which, if burnt, would develop a quantity of heat equal to that derived from the combustion of eighteen billion tons of coal.

* * * * *

In a few exceptionally favorable locations it is feasible to utilize a trivial fraction of the total energy of the tides.

* * * * *

Of extraordinary interest to chemists are the accumulating evidences of the inconceivably great amounts of kinetic energy possessed not only by radium, but by ordinary matter as the constitutional energy of its atoms.

* * * * *

Our civilization will be based on coal for many generations to come, in spite of tendencies which seem to imply that the burden is shifting to petroleum. However far the transfer may proceed, the carrying power of petroleum is temporary and likely to be brief.

The speaker then cited statistics showing the available coal supply in various parts of the world. He also referred to sources of natural gas and the wasteful methods in obtaining it that have led to a speedy reduction of the amount available. In speaking of our petroleum resources Dr. Little said:

As in case of natural gas, our reserves are rapidly nearing depletion and can hardly maintain our present rate of production for more than twenty years. We have wasted more than we have used. Our 260,000 producing wells leave more than half the oil under ground, and less than half of what they take out reaches the pipe line. Then we burn half of that as a substitute for coal, of which we have 6000 years' supply. We need an intelligent economic policy in these United States and power to enforce it. The basic cause of this orgy of waste and the unrestrained production that makes it cheaper to burn oil than coal is the small individual holding. The owner *must* hustle to get his oil out, or it will be taken by others from under his feet.

In summing up the situation, Dr. Little said:

Since coal must remain for generations our chief energy resource the line of progress parallels the better utilization of coal. Here a vast deal may be accomplished. Coal should be better cleaned. It should be fired under close scientific control. Heat losses should be minimized; power generation should be centralized, and small plants encouraged to buy their power. Inferior fuels should be utilized as powdered coal. The beehive oven should go. Coal mining should be integrated. We may expect notable developments in the processing of coal and the more effective utilization of coal products.

* * * * *

As the cost of human energy goes up that of the energy derived from nature must come down if social progress is to be maintained. Energy is the economic support of progress. If that support is to be adequately afforded we must have cheap energy. We can have cheap energy by better administration, better development, better application. With cheap energy we need common-carrier transmission lines, like those contemplated by the Superpower Survey, to make that energy available over wide districts.

The next speaker was Dr. Leo H. Baekeland of New York, whose subject was "Human and Superior Direction of Power." In this address the speaker first reviewed the relation of the chemist to the engineer, pointing out how they approach tasks from different angles and how the one often succeeds where the other fails. He then took up the question of industrial research as follows:

To the wide-awake manufacturer, the present industrial depression should be an incentive to engage more chemists, to do more chemical research work, instead of laying off the men of their chemical staff, as has happened in too many instances since we got out of that fool's paradise of so-called "prosperity."

Most of our industries badly need "fertilizing," and fertilizing is better done while the land lies fallow than during planting or harvesting time.

Whenever I see such shortsightedness which is bound to stunt our industrial efficiency for the future, then I wonder whether some of the financial or business men at the head of large industrial enterprises are not occupying their positions on an assumed and unearned reputation.

Dr. Baekeland then discussed the natural resources of America, referring particularly to coal and petroleum. He also referred to the tremendous possibilities for the utilization of alcohol in industry. His comment on this subject follows in part:

Industrial alcohol is another chemical industry in the United States which seems susceptible of an incomparably wider development as soon as it is less hampered by fanaticism in a more efficient commercial production and easier distribution. Most people cannot see in alcohol anything but its use or abuse as a beverage.

And yet, outside of such uses, there is hardly a chemical susceptible of wider and more beneficial application in the arts, the industries and the household economics. Its value as a solvent, its use in varnishes, artificial leather, smokeless powder, is well known among chemists. But a much more extended use is possible as a liquid fuel. The fact that it is far less volatile than gasoline and mixes readily with water, makes it not only cleaner, but incomparably less dangerous, whether it be used in the household for heating or illuminating purposes, or whether it be used on a motor car or a motorboat, or stationary engine.

Furthermore, its sources of supply embrace all inexpensive starch- or sugar-containing vegetables as well as the waste of our sugar refineries, all products of which this country has a prodigious supply. Converting our perishable farm products into products like alcohol, which can be stored indefinitely and of which the transportation and handling are easy, is one of the ways of equalizing the uncertain fluctuations of the yield of our crops.

Long after every drop of petroleum or gasoline shall have been extracted from our wells, every yearly agricultural crop will insure us a new supply of this valuable liquid fuel obtained by fermentation of starch- or sugar-containing liquids. I know

of no country where there is such an abundant source of supply, as well as industrial opportunities in conjunction with an abundant market within easy reach provided industrial alcohol can be furnished to the consumer at a low enough price.

But unintelligent application of the Prohibition Act will offset all this, whatever good effects it may try to accomplish in other directions, by putting unnecessarily exaggerated restrictions or handicaps upon the manufacture or distribution of industrial alcohol.

Few people realize that the price at which alcohol can be delivered to the consumer at a profit is considerably influenced by whatever unnecessary red tape impedes transportation or distribution. The well-intentioned manufacturer, who is endeavoring to lower the cost of production, feels his efforts rather futile when they are wiped out at the selling and distributing end.

If every annual crop of starch- or sugar-containing plants can furnish us an abundance of liquid fuel and solvents under the form of alcohol, we may look at this from another point of view and call it simply the stored up energy of the sun. The photochemical action of the sun rays under the influence of the chlorophyll, or green matter of the plant leaves, brings about the most subtle creative chemical synthesis. Carbon dioxide, a product of combustion, one of the ultimate destruction products of plant or animal life, combines with water under the action of sunlight. The first, or one of the first products of this synthesis is formaldehyde; the latter, in its turn, inaugurates a succession of further chemical syntheses which result in the formation of sugars, starch, cellulose, and other carbohydrates. No sun, no photochemical synthesis, no crops—no life! So that, after all, the whole living world is dependent upon a delicate photochemical reaction. Starvation on one hand, or abundance of crops and foodstuffs on the other, all within the range of photochemistry.

So here is a power, an energy, which has been much neglected by scientist and engineer alike. Where is the Faraday, the Ampère, the Leonardo de Vinci, where is the Archimedes who shall show us how to use the sun rays for charging our electrical storage batteries, or who will teach us how to handle the photochemical action of sunlight, to emulate nature in her delicate synthesis of plant life? Who will utilize this delicate method instead of our hitherto brutal processes of synthesis? Nature in her methods of plant life synthesis does not treat with boiling solutions or alkalies or strong acids; she uses no high temperatures or strong electric currents. If we want to be successful in this direction, we shall have to utilize equipment possessing large exposed surfaces similar to the leaves of plants. We may have to operate in rather dilute solutions instead of the concentrations which are ordinarily used in our present methods. We may have to find means for rapidly separating the formed products as fast as they accumulate. We may be compelled to work within narrow ranges of temperature, perhaps not exceeding those outside of which plant life stops.

But who knows what surprises are in store for us and how we may simplify all this after the subject once begins to receive enough attention

Dr. Willis R. Whitney was called upon by President Smith to address the audience on "Theories." He spoke, in part, as follows:

I want to have agreement as to what I mean by theory. It may be that scientists have become hardened to a special use of the word. So I define theory as mental concept as distinct from practice, which is always material. But for the scientist the combination of these two is necessary. They may be antithetical, but they are *not* antagonistic. As allies, they are invincible. A theory is a means of satisfying the mind, when, for sake of economy, order, and mental increase, various thoughts first form into a conjecture, then into an hypothesis, and then into a full grown theory.****Even unproved theories have value, and the value consists in something more than the pleasure the theorizing process gives to the theorist. A theory is more than a systematic generalization furnishing the most satisfactory account and a rational explanation of things, because it is always an incentive for further experiment. It is more a gathering of force preparatory to a jump.

* * * * *

We are increasing rapidly the measured area of natural phenomena, and this is being done by the application of theory. We plot our new facts on the old coördinates, and find them to be extensions of previous curves, and so we naturally continue to predict the location of new facts on the extension of known curves.

Dr. Whitney reviewed the history of theory, showing how it was a part of the mythology of ancient peoples. He then continued as follows:

There are big theories and little theories, proved and discarded theories, but we must not admit that there are useless theories. It is so difficult to acquire the habit of theorizing, and it is so seldom encouraged or produced or taught, that there is little danger from useless theories, if any exist. They are perhaps bad when they cease to live. A theory materializes only by and in accord with truth coupled with good works. A good theory is proved by its fruit, but you cannot prove a bad theory at all. You disprove it. In the undertaking you are sure to disclose new truth, and this is ample warrant for its existence. A theory does not grow at all except by the addition of newly assembled or discovered truth. That one theory is abandoned for another is not much more remarkable than that every time a new layer of brick or stone is laid over an old one, the latter ceases to be the top of the wall.

* * * * *

Probably no theory has had a longer life, or shown more valuable results than the atomic theory of the chemist. That is a product which dates from the mythical past, but no chemist can practically get along without it. Chemical understanding is built upon it. If it were nothing more than a system which enabled us to remember better the countless facts of our science, it would be well warranted. But, like almost all theories, it has enabled the chemist to prophesy and to produce. It has also led to extensions in kind, so that to-day we are recognizing that electricity must be added to our atomic theory, and that, through the combination, there comes an added systematic arranging of myriads of facts which the original atomic theory and separate electrical theories never contemplated. This, in turn, permits of still more prophecy and experimenting.

Shall we undervalue unproved or wild theories, such as that which bears on the enormous source of energy sometime to be made available through atomic disintegration (a theory of Soddy's)? Certainly not! How, then, may we distinguish the God-given from the earth-born conceptions? There may be no a priori way, but there are two ways which are usually successful. One is to see if the theory originates in someone who has actual understanding contact with the matter in hand, and the other lies in the application.

* * * * *

We have all recently received a letter from President Smith, describing the serious need of the dye embargo bill and of helping congressmen to understand the magnitude of the danger we run. This is a practical matter. "England, France, Italy, and Japan have already safeguarded their dye industries." The dye industry is the key to present and future explosive and munition developments, and promises to remain basic for future agricultural fertilizer undertakings. It is behind all research in medicines, deadly gas warfare, etc. It is not so much the value of the colors, but a much more extensive interest which concerns us. What has theory to do with that? Just this! The world owes the present stand of organic chemistry to a beautiful combination of theory and experiment. We now see it plainly in this industrial situation. In 1856 Perkin produced the first artificial dye. At that time, Kekulé was theorizing, and he then laid the foundations of all our modern structures. His theories, which soon led into the wonderful conception of the benzene ring, are now the ABC of the dye industry. I can't refrain from pointing to the value of theory in this case, or from adding that there is a lot of similarity between the taking apart and putting together of a clock and all the work which Kekulé and his followers have done. Most of the greatest nations of the world are still fighting for portions of the product of organic chemical theory.

Dr. Smith then introduced Sir William J. Pope, president of the Society of Chemical Industry of Great Britain and professor of chemistry in Cambridge University, who addressed the gathering on "Chemistry and Life."

Quotations from this highly interesting address follow:

Although chemical science has developed gradually and continuously and without any marked break of continuity during more than a century past it is possible to discern the existence of a progressive change in the character of the practical methods applied by the chemist. This is especially the case in connection with organic chemistry. In early days, discoveries were made largely as the result of acts of violence perpetrated upon chemical materials; delicate organic substances were distilled through red-hot tubes and indeed the most ordinary weapons of chemical research were those in which energy at a high potential was employed. During the last fifty years the organic chemist has forged for himself new tools in which low potential energy is applied; we are now in possession of numbers of stock methods of working in which the temperature changes concerned are very small and in which low potential energy is induced to take a part by the presence of a so-called catalyst.

The newer and less violent chemical methods have supplemented the older ones in an extraordinary degree and our knowledge of the science of organic chemistry has grown out of all recognition during the past half century; apart from this, however, the direction in which experimental methods have developed presents another aspect of great significance. The chemical methods by which plants and animals conduct their laboratory operations, by which they absorb their food and by which they elaborate highly complex organic compounds, are invariably methods in which low potential energy changes are involved; no considerable temperature variations are permissible and, in fact, the animal organism dies as a result of temperature fluctuations of but a few degrees. It is obvious that organic chemistry is approximating in its experimental methods to those which occur exclusively in plant and animal life; the ultra-modernity of the chemistry of vital processes becomes the more evident when we reflect that these processes are carried on in colloidal media and are brought about by the agency of catalytic agents. Notwithstanding the early recognition by chemists of the importance of colloids and of catalysts, the systematic study of these potent agents is of comparatively recent date.

The speaker then called attention to the operations performed by an ordinary plant leaf and laid stress on the fact that little progress has been made by scientists in emulating the chemical reactions taking place in plants.

"When we possess full working details concerning the plant leaf process for converting carbon dioxide and water into formaldehyde and oxygen by utilizing the sun's energy," said Sir William, "when we can make indigo and quinine by the identical methods adopted by the plant, chemical technology will be an entirely different proposition from the one which it now represents. Not that it is likely that we shall desire to replace the laboratory of the living organism as a source of natural products; it is difficult to believe that the indigo plant, properly developed and properly worked up, is not capable of competing successfully with coal tar as a source of indigo. The elucidation and imitation of plant and animal chemical methods will, however, provide us with means for manufacturing vast numbers of products which are unknown in nature, because the lower creation has no need of them; we are nowadays so far from nature that many such products may be of the utmost value to modern civilization."

The speaker also referred to the utilization of vegetable matter as a source of alcohol and oils for possible use as fuel. He spoke of the problems confronting the chemist in connection with the proper utilization of our stores of nitrogen compounds. Finally he called upon chemists to take advantage of their opportunities and concluded with these words:

We must, indeed, recognize that wide economic differences exist between a self-contained European country and others which have the whole tropical world within their range, and that entirely distinct types of problems are in consequence presented to the chemical technologies of the two species of nation. It is for us to realize all the bearing of these differences upon chemical science and chemical industry and to see that we neglect no means for applying the great opportunities within our reach in the service of mankind and of our respective countries.

Dr. C. E. K. Mees of Rochester, N. Y., was the next speaker. His subject was "Research Applied to the World's Work." He said in part:

During the last few years the great advantages of industrial scientific research have been recognized by the technical industries throughout the world, and laboratories have been established in connection with the industries in all countries. The establishment of these laboratories has taken different forms in different countries, and I do not wish at the present time to discuss the relative advantages and disadvantages of the various schemes which are being tried for the extension of industrial scientific research, but it may be desirable to consider for a few minutes the functions of a research laboratory in an industry.

The function of a research laboratory may be summarized as being to supply the technical information on which an industry is operated.

In fulfilment of these functions a research laboratory will draw for its technical information on the published literature, on its own records of previous experiments, and on direct experiments undertaken for the purpose of obtaining the information required.

* * * * *

The function of the laboratory in relation to the industry as a whole may be compared to that of the Intelligence Department of an Army. It supplies the information on which the decisions are made. These decisions are, of course, both positive and negative. It is the business of the laboratory to point out the direction which development should take and to lay down the conditions within which experimental work on new processes, apparatus, or materials should be limited, to watch possibilities for the new uses of materials and to encourage such possibilities where they appear, and finally to guard by advice based on positive information against misdirected experiment or development, or the purchase or exploitation of processes which will not eventually prove profitable.

The research laboratory is sometimes looked to as a source of shortcuts or convenient methods, and still more frequently reference to it is postponed until trouble actually arises, but it will not fulfil its functions in an industry and will not justify the expectations which may properly be entertained with regard to it until it is the center of technical information for the industry as a whole and is referred to continually on all technical matters.

"The Problem of Diffusion and Its Bearing on Civilization" was the title of the next address, by Professor Ernst Cohen of the University of Utrecht, Holland. Professor Cohen spoke extemporaneously. In a few words he called attention to the work of Abbé Nolet, Graham, Traube, Pfeffer, de Vries, Donders, Hamburger, van't Hoff, Arrhenius, Nernst, Jacques Loeb, and H. N. Morse to indicate that practically all nations have contributed to the present state of our knowledge of diffusion. He traced the development of the science of diffusion from the first recorded observation of this phenomenon to the present day and indicated its importance not only in physical chemistry but in biology as well. He then pointed out that, according to experiments conducted at the University of Utrecht, all of the diffusion coefficients so far determined are faulty in that they have been worked out in buildings not free from vibration. An apparatus based on the principle used by Prof. Julius of Utrecht, for the suspension of galvanometers, has been constructed for redetermining these diffusion coefficients in different media with the elimination of vibration, and results that are accurate to about 0.2 per cent are being obtained. Such accuracy is necessary for a further study of the laws of diffusion.

The final contribution to the program was the address of Prof. Wilder D. Bancroft of Cornell University on "Catalysis: The New Economic Factor."

The following excerpts are taken from this address:

If the world is going to recover in any reasonable time from the material losses of the recent war, some method must be devised for replacing the lost capital reasonably rapidly.

* * * * *

So far as I can see, the best hope for a speedy return of general prosperity lies in the intensive development of chemistry. The chemists must develop methods of increasing the production and decreasing costs. The most promising way of doing this is by a better utilization of the possibilities of catalytic action. As you know, a catalytic agent is one that in some way speeds up a reaction without necessarily being changed itself. Speeding up a reaction means increased output in the same time and perhaps the possibility of using a cheaper raw material.

The organic chemist is only just beginning to use catalytic agents with zest and we may expect at any time to hear of improved methods of manufacture such as the recent synthesis of maleic acid from benzene. The problem of a future supply of motor fuel is a very serious one. One of the preceding speakers, Mr. Little, believes that the solution lies in the hydrogenation of coal. Others think that a better yield of alcohol by fermentation will solve the problem. Still others hope to prepare some different combustible liquid from tropical vegetation and from cornstalks. I do not know which is the right solution or whether these three and still other methods will contribute in maintaining an adequate supply of motor fuel; but all that have been suggested require the use of catalytic agents.

If we could produce what is popularly known as cold light, equaling the firefly without adopting his methods, that would make possible an enormous decrease in the power necessary for lighting purposes. Cold light will come some day and we know enough now to predict that we shall make use of a catalytic agent to speed up the reaction which gives rise to the light. If we could cause the rain clouds which now pass tantalizingly over many of the arid regions to precipitate, we could increase the fertility and consequently the value of these lands to an unbelievable extent. This is not "rain-making" in the popular sense; but is a matter which is quite within the limits of accomplishment.

I do not know to what extent or when the chemist is going to make available the energy in the sunlight or the atomic energies which have been made manifest to us by the properties of the radioactive substances; but I do know that these things, when they come, will involve catalysis. It is because we cannot speed up atomic disintegrations that we cannot utilize the energy locked up in the atom. Vitamines are a mysterious set of substances which certainly act catalytically if we make our definition broad enough. I do not see how they can ever be used to generate power directly; but we are only just beginning to appreciate the part they play in the health of the individual. If we can raise the standard of general health and can decrease the amount of sickness, we shall have done more for the happiness and prosperity of the world than could be accomplished by almost any accumulation of capital. This is one of the most important of the problems that confront the chemist.

I have, of course, kept one of the very interesting theoretical points for the last. Sabatier in France has opened our eyes to the extraordinary possibilities which catalytic agents have in helping us to make organic compounds. J. J. Thomson in England has proved that catalytic agents may displace equilibrium, contrary to what has been believed as dogma by Ostwald and his school in Germany. Reid of the Johns Hopkins University has apparently furnished the missing experimental proof. He passed a mixture of the vapors of ethyl alcohol and acetic acid for twenty-four hours over silica gel as a catalytic agent and during the whole of that time he obtained about ten per cent more of ethyl acetate than corresponds to the theoretical equilibrium. These experiments have not yet been repeated by anybody else and there is always the possibility of an unsuspected error. The results seem to me theoretically possible and I should like to have you consider what they mean in case they are confirmed. Of course nobody cares about an increased yield of ethyl acetate; but think what a displacement of ten per cent in the right direction would mean in the synthesis of ammonia, to take a single instance! It would revolutionize everything. Such a thing may not be possible but it looks as though this was a legitimate scientific dream to-day and the legitimate scientific dreams of to-day are the successful technical processes of to-morrow.

In a recent report I expressed my belief that the formation of the National Research Council had put the scientific leadership in this country in the hands of the chemists. Nobody denies that the recent war was a chemists' war. I say to this audience that the world has a right to look to the chemists for even more help in the time of peace. We need not fail and we must not.

Side Lights

Analysis of the list of registrations to Friday noon, September 9, gives the following attendance figures:

REGISTRATION BY STATES

Alabama	1	Ohio	50
Arkansas	2	Oklahoma	1
California	9	Pennsylvania	113
Connecticut	45	Rhode Island	4
Delaware	17	South Dakota	1
District of Columbia	62	Tennessee	6
Florida	1	Texas	4
Georgia	3	Vermont	2
Illinois	45	Virginia	7
Indiana	7	Washington	3
Iowa	5	West Virginia	4
Kansas	3	Wisconsin	13
Louisiana	8	Wyoming	1
Maine	1	China	1
Maryland	33	Japan	4
Massachusetts	75	Holland	1
Michigan	14	India	1
Minnesota	5	Sweden	2
Mississippi	1	Porto Rico	1
Missouri	10	South America	1
Montana	1	Canada	3
Nebraska	3	France	1
Nevada	1	Philippine Islands	1
New Hampshire	5		1212
New Jersey (exclusive of New York Local Section)	37	Members A.C.S. and S.C.I.	1212
New York Local Section	512	English and Canadian guests	62
New York (exclusive of N. Y. Local Section)	72	Guests	255
North Carolina	6	Later Registrants	28
North Dakota	3	Total Registration	1557

The need for standardization is spreading to chemical courses in our colleges. If the newly created section on education does nothing more than to stimulate activity along the line of bringing chemical training in all universities up to a definite minimum standard, it will have done tremendous good to the cause of chemistry in America.

The "special story" writers of the various New York newspapers were very much in evidence. The scientific accuracy of their "stories," which appeared throughout the week, was refreshing. No doubt it was also a treat for those who were quoted to read the descriptions of themselves as viewed through the eyes of newspaper men. For instance, "Bannie" was described in one article as a chemist who did not answer the usual description of the laboratory hermit, but had rather the appearance of a well-dressed business man.

Whatever system had been devised for intercommunication between divisional and section meetings failed to function. Not only were the attendants at one meeting kept in ignorance of what papers were being read at the other meetings, but if one happened to come in during the session of a meeting there was no indication as to who was speaking or what paper was being presented unless one happened to know the speaker. Every meeting room was fitted with blackboards, chalk and in most cases telephones. There was a short circuit somewhere.

The foregoing remarks lead to the general observation that no entirely satisfactory method has yet been devised for giving members an opportunity to hear particular papers in several meetings. As one member expressed it: "I wasted one morning trying to get to several divisions at different times to hear papers in which I was particularly interested. Since then, I have stayed in the division covering my specialty from start to finish." Maybe that is the solution because of the many divisions that are in session simultaneously, but we would hate to admit it.

There is a great difference between meetings of the SOCIETY held in large cities and in cities of moderate size. Each has its advantages, but the "one big family" idea cannot be worked out satisfactorily in cities like New York and Chicago. Possibly the change is a good thing. We might soon tire of meetings if they were all similar in character.

The advance posters of the Smoker looked very promising, but many of the principal acts failed to materialize, due to faulty imagination of the audience. Nevertheless, the understudies provided an evening of splendid entertainment and the advertised program could hardly have been better.

Sir William J. Pope's contributions to the General Meeting and the International Meeting were worthy of the high esteem in which he is held by chemists everywhere. His presence, together with that of his distinguished colleagues, helped materially in cementing more closely the ties between the chemists of English-speaking nations of the world.

Professor R. F. Ruttan, who headed the delegation of Canadian chemists, is no longer a stranger at A. C. S. meetings, having attended the Rochester convention last spring. His contribution to the program of the General Meeting gave an indication of the strides our neighbor to the north is making in developing and coördinating her chemical industries.

The meetings of the SOCIETY held this year were unusual in their importance. Particularly is this true of the New York meeting. In addition to the scientific aspects, the public aspect had to be kept in mind continually, for the public is now greatly interested in chemistry and understands the broader application of our science to a greater degree than ever before.

Members of the New York Section seem to be more modest than those of other cities. They hesitated to identify themselves with special ribbons or badges as has been the case with local sections in other convention cities. It often occurred that a member from one part of the country would ask someone who looked like a New York member something about directions or locations of places of interest, only to be met with a pleasant smile and "sorry, but I am from out of town myself."

All of the divisional meetings were remarkably well attended and spirited discussions were the order of the day. It frequently happened that discussions had to be limited to a few minutes on the part of each speaker in order to conserve time for the remainder of the program, and in several instances all of the papers could not be read for lack of time.

The use of the Columbia University dormitories was a welcome courtesy on the part of the university authorities. Only those who were compelled to travel back and forth from downtown hotels to the meeting rooms can fully appreciate it.

SEVENTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

A policeman stalked into the office of the Manager at 1:30 P.M., on Monday, September 12, 1921, and announced that the crowd outside clamoring for admission was every minute becoming greater and more difficult to handle. He urged that the doors be opened at once to avoid trouble. It was done, though the Exposition was advertised to open at 2 P.M. Thus at the very outset were dispelled the fears of those who had predicted that the holding of this great medium of business enterprise and public education in so distant a part of New York City as Kingsbridge Road and Jerome Avenue in the Bronx, where the Eighth Coast Artillery Armory is located, would be unsuccessful.

A wonderful picture was presented on entering the building. A great array of booths filled with carefully and thoughtfully prepared exhibits in the many lines of industrial effort which go to make up the chemical industry in its entirety met the eyes. The temptation to plunge at once into an inspection of the individual displays was resisted, for we wished first to get the impression of the Exposition as a unit. Fortunately fine opportunity for gaining such an impression was afforded by the balcony which encircled the upper part of the building. Looking across the rows of exhibits a deep impression was made, but the full meaning of it all was not gained until we walked across to one end of the balcony and gazed down upon street after street of exhibits, a multitude of visitors within the booths and filling the aisles. There in that great space, some 600 feet long by 250 feet wide, was housed on one floor the Exposition. It was estimated that when a visitor walked continuously the full length of each aisle the journey covered a distance of one and one-fourth miles. This space was filled with the displays of 424 exhibitors. The total attendance during the week was 120,081.

While waiting one evening for the arrival of a prominent speaker we studied the faces of the steady stream of visitors entering. It was inspiring to note the high average of these visitors and the uniform expression of thoughtful and earnest studiousness. Men and women alike had undergone the tedium of a long journey from the further parts of the city and visitors had come from many miles away really to learn something of the intimate character of the fascinating story of chemistry.

Individual Exhibits

Coming down to the main floor and purposely wandering indefinitely through the aisles we came away with certain general impressions. In the first place, a new departure had been made in placing upon the walls in easily legible characters quotations which told of the spirit imbuing the chemical industry, of the needs of the industry, and of its bearing upon the public welfare. Then, too, it was apparent that exhibitors were making much larger use of graphic methods of telling the story of their processes so that any layman could understand. These efforts were supplemented by well displayed products, by model machines, and by full scale normal operations. In the center of the exhibits stood out the group of companies constituting the Allied Chemical & Dye Corporation. In one of these, that of the Solvay Process Company, was shown a photograph of the plant for nitrogen fixation which has recently been put into successful operation on a commercial scale.

We give the first prize for artistic beauty of display to the Nichols Copper Company. It was a real artist who designed this entire booth.

A constant stream of interested visitors in the booth of Arthur D. Little, Inc., showed what an effective hit Dr. Little had made in arousing public interest in the infinite possibilities of the chemist's power as shown through the display of a silk purse made from the ears of sows, as duly attested by affidavits framed and placed nearby. Thus was disproved an adage which has come down through the centuries.

It was interesting to note in the exhibit of the Florasynth Laboratories products bearing the characteristic labels of the American Medical Association, testifying that these products met the requirements of that Association as to purity.

The display of the Coors Porcelain Company aroused a feeling of pride in American ability, especially if one knew the fascinating story of the development of this industry of our Southwest. More interesting than the exhibit itself was the information gained that despite the delay in legislation, American consumers are standing loyally by this war-born industry.

In full keeping with the spirit of the previous two weeks the Canadian government and Canadian industries were thoroughly represented by displays of the natural resources and available power of this good neighbor of ours.

It was in the booth of the National Lime Association that one of the most interesting charts was shown. By most of us lime is thought of as going chiefly, so far as tonnage output is concerned, into building operations. But here it was shown that considerably more than half of the lime produced in this country is utilized in the chemical industries. Further the chart showed the manifold applications in industrial chemistry of this cheapest of all chemical bases.

The subject of alcohol as a chemical reagent in contradistinction to its use as a beverage has been widely discussed within recent months. These discussions were forcefully supplemented by the adjoining exhibits of the U. S. Industrial Alcohol Company and the U. S. Industrial Chemical Company.

It was a matter of regret that only one of the railways of the country—the Southern Railway—exhibited specimens of the natural resources along its lines. This important feature of earlier expositions should be revived and developed to the utmost.

The ceramic industries so essential to chemical development were present with full line displays, showing the remarkable strides which have been made in taking care of the needs of the chemist. So, too, machinery exhibits were everywhere interspersed, an almost bewildering multitude of appliances giving clearly the idea of the intricacies involved in many lines of chemical manufacture.

Full advantage of the Exposition was taken by the many scientific societies and the technical and trade publications which contribute so much to the industry.

The Bureau of Standards as usual presented an extremely instructive exhibit, setting forth the many points at which it serves chemistry—publications of all sorts, scientific instruments of precision, and many other features of its valuable work. It is to be regretted that the Bureau of Foreign and Domestic Commerce could not take the Exposition more seriously, for opportunity was here afforded to establish a firm and intimate relationship between that important branch of government work and the efforts of our chemical manufacturers.

Formal Addresses

The formal addresses in connection with the opening of the Exposition took place on Monday evening, September 12, in the auditorium. On the speakers' platform were United States Senator Irvine L. Lenroot, Brigadier General Amos A. Fries, chief of the Chemical Warfare Service, Col. E. S. Austin, commanding officer in charge of the armory building, Dr. Chas. H. Herty, chairman of the Advisory Committee, and Mr. Charles F. Roth, of the Exposition Management.

In opening the exercises Mr. Roth spoke of the growth of the Exposition and of its value both to the development of the chemical industry and as an effective aid in public education as to the meaning of chemistry. He introduced Dr. Herty, who spoke briefly of the necessity of an industry complete in every part and thoroughly unified in the spirit of service to the country.

In introducing Senator Lenroot, Dr. Herty mentioned the special appropriateness of having Senator Lenroot make the principal address in connection with the opening of the Exposition, as his position on the Military Affairs Committee of the Senate had led him to study carefully all questions affecting the Chemical Warfare Service of the United States Army.

Senator Lenroot spoke as follows:

The Relation of Our Chemical Industry to Our National Defense

By Senator Irvine L. Lenroot

I was very glad to accept the invitation to make the opening address at this important Exposition not primarily because of my interest in all fields of activity that make for progress of our country but because of my conviction that the future safety of our country from hostile attack lies in the development of our chemical industry, and I have chosen for my subject to-night "The Relation of Our Chemical Industry to Our National Defense." As a member of the Committee on Military Affairs of the Senate, it has been my duty to study the question of National Defense and its cost to the taxpayers of America. It was not very long before I became especially interested in our Chemical Warfare Service and what we might hope for it in the future if properly supported. I found that thirty per cent of our casualties in the war came from German gases. I found that, although heretofore generally condemned as cruel and inhuman, results showed that casualties from gases were no more cruel than those from any other method of attack. I found that the cost of preparedness through chemical warfare, the aeroplane and the submarine was the merest fraction of the cost of a large standing army, dreadnaughts and battleships and heavy ordnance. I found although limitation of armaments may be agreed upon, and I hope will be agreed upon, chemical warfare is of such a nature, involving so little in personnel or cost of material that it would be folly for any nation to rely upon any international agreement that poisonous gases should not hereafter be used in war.

The Importance of Chemical Warfare

Who won the war may be argued for the next generation, but the chemists of America and of our associates in the war have not received their due share of credit. But for the chemists of Germany she would have lost the war before we got into it. Had it not been for her progress in chemical industry she could never have secured sufficient explosives to save herself after the blockade was established against her. Had it not been for the chemists of the allies meeting discovery with new discovery Germany would have won the war.

The progress in chemical warfare since the armistice has been remarkable and too little realized by the people of the United States. Because of the advance made in explosives and gases and the development of the aeroplane I verily believe the battleship has become obsolete, and that it is a waste of money to go on constructing them. This was proved, it seems to me, in the recent bombing tests, but only a part of our resources were then employed or could be employed. With an enemy crew aboard, with the dropping upon them of gases as well as explosives, their doom would be absolutely certain. The aeroplane, the aeroplane carrier, the submarine, gases, and high explosives will be the implements of war of the future. We may agree upon a limitation of battleships, a limitation of submarines, a limitation of aeroplanes, a limitation of armies, a limitation of the quantity of the war material that can be kept on hand, but we cannot agree upon a limitation of brains, and if we could the limitation would be worthless. We must also understand that any agreement which may be entered into will be binding only upon honorable nations who may assent to it. If at any time one nation may desire to steal the property of another a written agreement not to use means which would enable her to do so will be worthless.

Let us hope that the conference to be held in November will mark the beginning of the end of large navies and huge armies, but let us not be idiotic enough to enter into any agreement that the scientists of the nation shall not employ their brains in research and development that will assist in defending our nation should any dare attack us.

Underwood and Underwood

SENATOR IRVINE L. LENROOT

Private Industry Necessary for Chemical Preparedness

We can be prepared to defend ourselves at practically no cost by the encouragement and development of the chemical industry. We have about one hundred and fifty chemists now at Edgewood Arsenal doing splendid research work. Private industry has many chemists also doing research work, but unless private industry can exist and prosper, finding a market for their product in commercial life, either the Government must employ more chemists or men will not enter that profession. Private industry engaged in chemical production will give us a reserve in chemists, but will also give us plants that can be rapidly converted for war purposes if the need shall ever arise. The Government in the last war spent hundreds of millions of dollars in new plants that would not have been necessary had the dye industry been as far advanced in the United States as it was in Germany.

If the dyes used in America are made in America we shall have the chemists and we shall have the plants that will make America so strong in defensive warfare that none will dare to attack us. We should remember too that if ever attacked again it is not likely that we will ever be in such favorable situation as we were in the last war. For two and one-half years we had been making explosives for the allies. Our chemists were employed in the development of high explosives before we declared war at all. We had two years and a half to prepare for that war before we did go in, and how poorly we were then prepared I shall not dwell upon to-night.

Protection of the Industry

There is some difference of opinion among the members of Congress as to the character of the protection which is to be given the dye industry, but I feel that the overwhelming sentiment in Congress is that this industry must be thoroughly protected. There are some who think this protection should be through the medium of import duties alone. If this plan is decided upon, I am confident that these duties will be so high that they will be practically prohibitive for the dyes American manufacturers are making satisfactorily and at reasonable prices. On the other hand, there is a feeling that a selective embargo should be enacted. Those who are opposed to the embargo plan base their opposition on the ground that they fear it will lead to monopoly. Personally I feel that this possibility of monopoly could be amply safeguarded by including in the legislation a provision giving to the President of the United States, whenever it might become apparent that monopolistic conditions prevailed in the industry, power to suspend this embargo legislation and if considered desirable to reduce the duties. I want to see this industry safeguarded and if there is a possibility of error in the form of the legislation to be enacted, I want it to be on the side of the American industry.

To conclude, I am convinced of two things:

1—The importance of chemical warfare, and the necessity for continued research and development.

2—The necessity of the encouragement of the chemical industry to insure a reserve of chemists, and plants that can be converted for the manufacture of explosives and gases should the need arise.

Let the nations of the world know that although without a large navy or army, while all our energies are being devoted along the paths of peace, nevertheless we are possessed of the last word in science and invention and are ready to use it—that we have the skill and we have the material to defend ourselves, then never again shall any nation look upon us with contempt or mock our ability to make war.

Let us agree to sink our battleships, melt our cannon, destroy our fortifications, if other nations will do likewise, but let us encourage rather than destroy progress in discovery and invention making for the happiness and welfare of our people in time of peace and for their defense in time of war.

. . . .

The final speaker was Brigadier General Amos A. Fries, who because of his efficient leadership of the Chemical Warfare Service and his active efforts in support of the chemical industry as a reserve for that Service, received a warm welcome from the assemblage. General Fries gave an interesting account of the developments in chemical warfare and concurred most heartily in the views concerning chemical warfare expressed by Sir William Pope at the meeting of the AMERICAN CHEMICAL SOCIETY during the preceding week. General Fries urged clear thinking on the part of the American people as to the exact status and significance of chemical warfare and insisted that unless adequate appropriations were made by the Congress, the work in this important feature of warfare would suffer severely.

The principal speaker on Tuesday evening was Congressman Fred S. Purnell of Indiana. Congressman Purnell gave a vigorous presentation of the importance of the chemical industry and of the necessity of strong Congressional support. He said in part:

> I think we are justified in saying that America has taken the lead in the world's chemical industry since the war. That position must be maintained, not only as a potential element of preparedness, but as a peace measure. The coal-tar industry and the science of chemical warfare are so closely related that it becomes our paramount duty to protect the American dye manufacturers. The military strength of a nation will in the future depend almost entirely upon its dye plants.
>
> America cannot afford to disarm unless we have a self-sustaining dye and coal-tar chemical industry. There are very vital reasons why we need a native dye industry. The Tariff Commission estimates that $3,000,000,000 worth of American goods yearly depend upon coal-tar dyes and their intermediates for their manufacture. Shall we again turn to Europe for these dyes, or shall we encourage their manufacture here?

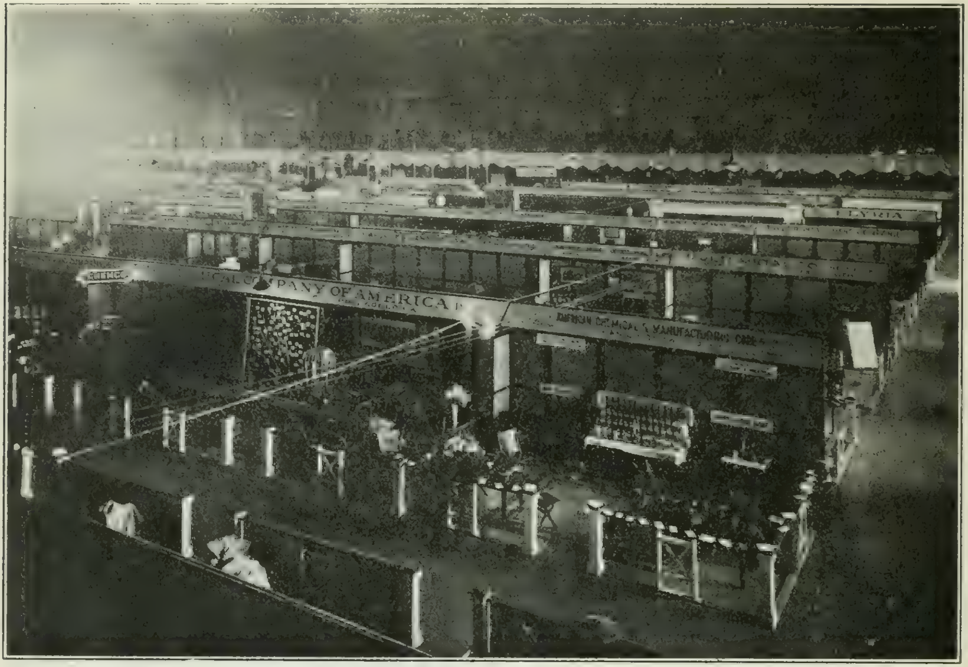
Mr. Purnell then quoted figures showing the output of coal-tar products in this country, stating that in 1915 there were only seven dye concerns in the country, with an output of 6,619,728 lbs., valued at $3,569,795, while in 1920 the number of plants had grown to 90, with an output of 88,253,776 lbs., valued at $95,613,749, and continued as follows:

> If we are to save this industry, we must act now. I find it hard to recommend an embargo, but unless we take effective measures now, it will be impossible to interest American capital in dye plants and the world monopoly in dyes will be returned to Europe.

A thoughtful address was made by Hon. Thomas Walker Page, chairman of the U. S. Tariff Commission, on Wednesday evening. Mr. Page held that the tariff had played no particular role in the past presidential election and that a definite line of settlement of tariff legislation by the present Congress was still a very uncertain matter. Undoubtedly there would be considerable delay before the tariff bill now before the Senate became a law. This is in no wise a reflection upon the ability of Congress to enact legislation promptly, but rather will be the result of the tremendous difficulties which must be overcome in the formulation of a tariff bill under present world conditions. Included among these the speaker mentioned: uncertainty as to the extent of protection needed in many lines of industry; difficulties in ascertaining costs of production (The Tariff Commission, said Mr. Page, had experienced these difficulties in its efforts to determine the cost of production of American dyes. Necessarily even greater obstacles must be encountered in establishing costs of production abroad.); differences of opinion as to what is raw material and what is finished products; and variations in depreciated exchange in foreign countries. Mr. Page felt that these questions had been handled only superficially by bankers and financiers and that the only measures adopted to date amounted to nothing more than mere postponement of evil. The speaker said that Schedule I (the chemical schedule) of the present tariff bill was by all means the best classified schedule presented in any tariff bill. The credit for this work he freely gave to the painstaking labors of Dr. Grinnell Jones, chemical expert of the Tariff Commission, and his associates.

He felt that one of the most important features of the new bill was the American valuation proposal and stated that studies were now under way to determine how this feature of the proposed law should be worked out.

The Commissioner resented in the strongest possible terms the criticism by congressmen that the census of dyes recently issued by the Commission was timed to influence legislation which would give to the Commission power to handle the details of dye importations through the acquirement of an appropriation of $100,000 for this purpose. He called attention to the careful studies the Commission had made and published from time to time during the past several years of the course of development of the dye industry, and stated that this census was published as soon as the information was compiled, in order to be of genuine service to Congress through the presentation of facts.



The Auditorium

Below the Exposition floor was the Auditorium, where for the first time adequate provision was made for the delivery of addresses and for the showing of industrial films. The noises were absent and the seating capacity was abundant and well arranged.

During the afternoons important symposiums were held in this auditorium on the following subjects: Crushing, grinding and pulverizing; industrial problems; evaporation and drying; paint and varnish; power plant in chemical industries; American dyes and colors.

When the formal addresses or symposiums were not being held there was a constant display of motion picture films, carrying the visitor through many of our most interesting plants, showing with faithful reproduction the magnitude and detail of operations. No more striking advances have been made within recent years than in the excellence of these industrial films. Especially noteworthy is the careful thought which has been given to the legends, which in nontechnical language, and without bombast, supplement effectively the high-class photography shown in the films. An interesting feature was the introduction of four-minute speakers who emphasized the present critical legislative situation confronting the American chemical industry. Concise and clear-cut addresses of this character were made by Mr. H. H. Dow, and by Drs. J. M. Matthews, H. E. Howe, R. H. McKee, Charles L. Parsons, and Charles Baskerville.

A double choice presented itself for the location of the Eighth Exposition in 1922, as the proposed conversion of the Grand Central Palace, the home of former expositions, into an office building had been abandoned. The management wisely decided to leave this decision to the exhibitors themselves. So a formal ballot was taken, as the result of which an overwhelming vote was cast in favor of the Grand Central Palace, the one objection to the site of the Armory being its great distance from the center of the city. Advance leasing of space for the Eighth Exposition is already a guarantee of its success.

As in previous years the press devoted much space to the Exposition and did a great deal to spread its influence to far wider circles than the actual visitors who attended.

Conclusion

Looking back over the week, what are the strong and what are the weak points developed by this Exposition? Certainly it has demonstrated the intricacies of the chemical industry, the dependence of each part on the other, and the necessity for continued closest coöperation. There was a time during the past year when some of the dye manufacturers felt that their industry should be set forth before the general public in a unified display of these products alone. Such a policy we are confident would have been a grave mistake, for the important thought for the general public to obtain is the multifold variety of lines of effort which characterizes the chemical industry as a whole. For this reason it was a matter of regret to learn that some of the exhibitors of machinery have been attacked by the same microbe and feel that machinery is so important that it should have a special and isolated display. It is sincerely to be hoped that such narrow viewpoints will not materialize in the breaking up of the present system of a complete survey of the industry. That is the picture which must be preserved. Departing from that policy, disintegration will soon be complete and the great opportunity for this unique method of industrial stimulation and public education will have been lost. It must not be forgotten that there are those who would like to see this agency crippled. It is squarely up to the various elements which contribute to the successful upbuilding of the American chemical industry to see to it that the sound policy, so effective in the past, shall be continued. America has led the world in the matter of chemical expositions. It must keep in the front.

Features of Exposition Week

AMERICAN CERAMIC SOCIETY

A conference of the officers and committee members of the American Ceramic Society was held Thursday morning, September 15, at the Hotel Commodore for a discussion of the program of activities outlined for the association by R. C. Purdy, the new organizing secretary. This program includes reorganization of the work of the divisions of the Society with the view of bringing about greater coöperation and better service to members; redistricting of local sections and encouraging them to greater activity; introduction of "trade paper" features into the Journal of the Society; relation with National Research Council and other scientific bodies; and finally, sources of revenue.

On Friday morning, September 16, special meetings of various committees of the Society took place, and on Friday afternoon the American Ceramic Society met at the Chemical Exposition. On the evening of the same day industrial moving pictures of the ceramic industry were shown at the Exposition.

The Friday afternoon session was devoted largely to the reading of technical papers. John G. Jones read a paper on "Business Conditions Relating to the Clay Working Industry" in which he outlined the apparent reasons for the recent depression in business and its effect upon the ceramic industry. He predicted better times ahead and urged the necessity for adequate protection for the American ceramic industry. The speaker touched briefly upon the effect of imports of chemical stoneware upon the ceramic industry.

P. C. Kingsbury delivered an address on "The Importance of Chemical Stoneware in the Chemical Industries." He emphasized the fact that an American chemical industry must not depend upon foreign supplies of chemical stoneware.

S. R. Scholes read a paper on "The Passing of King Methane." Fred B. Jacobs spoke on "Reducing Manufacturing Costs with Grinding Wheels." Charles F. Binns spoke of the advantages of porcelain laboratory ware and the progress that has been made in the American porcelain laboratory supplies industry. Other papers presented were: "Art Division Research Suggestions," by F. H. Rhead; "Refractories," by J. Spotts McDowell; and "Heavy Clay Products Research," by M. B. Greenough.

....

ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS

About sixty chemists responded to an invitation sent to representative textile chemists in eastern states to attend a meeting at the Chemists' Club, New York, Tuesday afternoon, September 13, to consider the formation of an association of textile chemists and colorists.

The meeting was called to order by Winthrop C. Durfee, who briefly outlined its purpose. Prof. Louis A. Olney, of the Lowell Textile School, was elected chairman of the meeting, and Walter E. Hadley, of the Clark Thread Company, Newark, secretary.

Prof. Olney spoke at length on the desirability of bringing textile chemists together for the periodic consideration of their special problems and suggested that this could be accomplished best by the formation of an association. He explained why it would not be feasible to organize as a Division of the American Chemical Society and outlined what he considered to be the objects of an association of this kind, as follows:

1—To promote the technical interest of its members in the properties and application of dyes and the processes of scouring, bleaching, and finishing.

2—To develop a closer relationship between theory and practice in the application of dyes and other chemicals used in the textile industry.

3—To serve the textile and color industries by developing standard methods of testing dyes and analyzing textile materials in general and of standardizing systems for these tests and recording their results.

4—To encourage research work along textile chemical lines.

5—To encourage and supervise the establishment of a complete textile chemical laboratory.

Prof. Olney suggested that the membership of such an association might be divided into three classes:

1—Regular or active members, who should possess as qualifications for membership a thorough technical training and at least five years of actual experience in textile chemical lines.

2—Junior members, who would include students and apprentices.

3—Sustaining or corporation members, who would include textile manufacturing concerns and also manufacturers of dyestuffs and chemicals used in the textile industry and who would be called upon to supply funds to support research work undertaken.

After considerable discussion of the subject presented by Prof. Olney a vote was taken to determine the interest of those present in the proposal. The vote showed unanimous approval.

There followed a general exchange of views regarding the scope and function of the proposed society, after which the meeting adjourned to reconvene in Boston during the week of the Textile Exposition, October 31 to November 5.

....

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

About 110 members of the American Institute of Chemical Engineers and guests, including representatives of the Society of Chemical Industry of Great Britain, enjoyed what has been characterized as one of the most successful of the annual "exposition dinners" of the Institute on Wednesday evening of Exposition Week at Hotel Commodore. The guests included the following English chemists: Sir William Pope, Charles S. Garland, Capt. T. J. Goodwin, William E. Jordan, S. W. Gamble.

Dr. David Wesson, president of the Institute, presided and, after the dinner, in his usual witty vein called on representative English and American chemical engineers for remarks.

Sir William Pope devoted his remarks largely to the question of education for chemical engineers and drew a comparison between the requirements of such education in England and in America.

Capt. T. J. Goodwin dwelt at length upon the value of coöperation between the chemical engineer group of the Society of Chemical Industry and the American Institute of Chemical Engineers. The hope was expressed that bonds between the chemical engineers of the English-speaking nations would be drawn closer as time goes on. S. W. Gamble was another of the English guests to be called upon.

The American chemical engineer and his work were discussed by the following members of the Institute: H. C. Parmelee, editor of *Chemical and Metallurgical Engineering*, Maximilian Toch, and J. C. Olsen, secretary of the Institute.

The attendance was larger than that of any previous banquet of the Institute and the presence of the distinguished visitors from abroad lent particular charm to the occasion.

....

SYNTHETIC ORGANIC CHEMICAL MANUFACTURERS

Eighty American manufacturers of synthetic organic chemicals met at the Pennsylvania Hotel, Thursday afternoon, September 15, to discuss questions affecting the general welfare of the industry they represent and to formulate plans for some method of import control, similar to the selective embargo, for the protection of the industry.

The meeting was called by the American Dyes Institute at the suggestion of several manufacturers of synthetic organic chemicals, some of whom are not members of the Institute.

The meeting was presided over by R. C. Jeffcott, of the Calco Chemical Co., and president of the American Dyes Institute. Dr. Chas. H. Herty, editor of THIS JOURNAL, was the chief speaker, and a round table discussion followed his remarks. Dr. Herty urged effective coöperation on the part of all manufacturers to perpetuate this industry in America. He emphasized the need for adopting a broad viewpoint on this whole question and subordinating individual selfish interests to the interest and welfare of the nation as a whole. It was pointed out that any organization of the kind in contemplation would die in early infancy if those participating had nothing but the success of their own particular business at heart. What should be done and what the nation demands, said Dr. Herty, is that in considering the organic chemical industry, it should be regarded as a national trust and as an asset to the nation and essential to the welfare of the people as a whole.

The work of the American Dyes Institute was commended very highly at the meeting and a committee was appointed to confer with the officials of the organization for the purpose of enlarging its scope so as to include all branches of the organic chemical industry.

The desire was expressed to form, in the near future, a complete organization of all American manufacturers of synthetic organic chemicals which would be effective in furthering the interests of this industry as a whole.

All of the interests represented at the meeting seemed to be in complete harmony on the objects sought. Another meeting will be held in the near future.

....

UNITED WAIST LEAGUE CONFERENCE

A conference of leading chemists, dyestuff producers, dyers, piece goods manufacturers and ready-to-wear manufacturers, held at the headquarters of the United Waist League of America on Tuesday, September 13, resulted in the appointment of a committee to "get to the bottom of the dye problem" which, it is hoped, will bring about a better understanding among manufacturers of dyes, consumers, and the public.

The entire dye situation was discussed from every angle by the representatives of the various trades and professions and a plan of action was agreed upon. It is proposed that the special committee, appointed for the purpose, secure samples of colored fabrics which are said to have lost their fastness. When the cause of the difficulty has been determined, action will be taken to prevent recurrence of the trouble.

The committee tentatively named to begin this work includes: Henry Blum, of the United Piece Dye Works; Dr. J. Merritt Matthews, of the American Dyes Institute; Williams Haynes, of *Drug and Chemical Markets;* Samuel Floersheimer, dress manufacturer; Henry Froelich, blouse manufacturer; J. Goldsmith, silk manufacturer; E. H. Killheffer, of Newport Chemical Works; Dr. L. J. Matos, of National Aniline and Chemical Co.; Mr. Muller, of the Textile Color Card Association; Mr. Craiger, a dyer; H. J. Kenner, of the Associated Advertising Clubs of the World; Mr. Nathan, a cotton goods converter; J. M. Reader, of the National Silk Dyeing Co.; M. Mosessohn, executive director of the United Waist League; and David N. Mosessohn, executive director of the Associated Dress Industries of America.

Dyestuff makers and dyers present at the conference gave an emphatic affirmative answer to a dress manufacturer who asked whether American-made fast colors can be obtained.

....

CHEMICAL SALESMAN'S ASSOCIATION

The Salesman's Association of the Chemical Industry was organized at an enthusiastic meeting at the Chemists' Club in New York, September 7. The first annual banquet of this new Association was held at the 8th Coast Artillery Armory in the Bronx on Thursday evening of Exposition Week.

Nearly 100 salesmen and sales executives connected with American chemical manufacturers or their agents attended the organization meeting, adopted a constitution, and elected officers for the year as follows: Burton T. Bush, of Antoine Chiris Co., president; F. L. McCartney, of Monsanto Chemical Co., first vice president; Theo. R. L. Loud, of New York Quinine Co., second vice president; Chas. B. Hall, of Cleveland-Cliffs Iron Co., third vice president; Williams Haynes, of *Drug & Chemical Markets*, secretary; A. A. Wasserschied, of Mallinckrodt Chemical Works, treasurer.

President Bush, in his acceptance speech, told of other industries that had benefited greatly from similar associations of salesmen because of the better feeling that grew out of a common interest in the organization activities. "No industry in America faces such development as does the chemical industry, and its future is largely in the hands of salesmen.

"This association," he concluded, "will give us a sense of belonging to something bigger than our own affairs; it will create esprit de corps. We are still competitors—friendly enemies—but we are all of one mind when it comes to the progress and the prosperity of our industry."

After considerable debate a motion that all chemical salesmen, including representatives of foreign manufacturers, be admitted to membership, was lost by unanimous vote, on the score that one of the prime purposes of the Association was to promote and guard the American industry as such.

The organization committee, to whose efforts the Association owed its formation, was made up of Fred E. Signer, of Butterworth-Judson Corporation, chairman; Williams Haynes, of *Drug & Chemical Markets*, secretary; Charles F. Abbott, of National Aniline & Chemical Co., Inc.; E. J. Barber, of The Barrett Company; John A. Chew, of the Warner Chemical Company; A. H. Pierce, of Grasselli Chemical Company; Edwin C. Scott, of Wing & Evans, and P. S. Tilden, of the du Pont Company.

BANQUET

About 200 members of the Association attended the banquet and enthusiasm waxed high. President Burton T. Bush introduced the speakers and in his preliminary remarks emphasized the need for coöperation among those connected with the selling organizations of the chemical industries and expressed the hope that the Association would assist in creating a better feeling among the representatives of various concerns.

Edward J. Cattell, statistician of the City of Philadelphia, delivered an inspiring address, replete with wit and old-fashioned common sense. John Jones, sales manager of the Alexander Hamilton Institute, predicted that business would be close to normal before another twelve months have passed. He emphasized the immense field that is opened to the chemical salesman because of the many contacts of chemistry with all sides of life. Mr. Jones also outlined the large part that chemistry plays in the peace-time industrial work of a nation and emphasized the need for making American chemistry and American chemical industries prominent in an international way as well as nationally. He further pointed out that nothing had ever been done on a world-wide scale without the backing of a strong organization with a well-defined plan of action. He, therefore, urged the members of the Association to outline a definite plan of activity which would eventually permit the American chemical industry to stand on its own feet and capture the chemical trade of the world.

....

CHEMICAL PLANT EQUIPMENT MANUFACTURERS

At a meeting of representatives of the leading manufacturers of chemical plant equipment at the Chemists' Club, New York, on Saturday, September 17, it was decided to form an Association of Chemical Plant Equipment Manufacturers.

The object of this association is to further various interests of these manufacturers, which, it is believed, can be promoted more satisfactorily by action as a group rather than as individuals. The following committee was appointed to take charge of organization: J. George Lehman, *chairman*, Bethlehem Foundry & Machine Co.; Paul O. Abbé, of Paul O. Abbé, Inc.; A. A. Holmes, of E. B. Badger & Sons; C. H. Kimberly, of Schutte & Koerting Co.; and P. C. Kingsbury, of General Ceramics Co.

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

Camphor Substitutes in the Manufacture of Celluloid[1]

By Albert Parsons Sachs and Oscar Byron

1523 Madison Ave., New York, N. Y.

The history of celluloid manufacture is so well known that to recount it here would be superfluous.[2] Alexander Parkes[3] observed that nitrocellulose, camphor, and alcohol are of service in the preparation of horn, rubber, and gutta-percha imitations. A few years later Daniel W. Spill[4] gave his famous formula for the gelatinization of nitrocellulose by ethyl-alcoholic solution of camphor, followed by kneading of the plastic mass between rolls. The Hyatt brothers[5] worked out the technical details for the large-scale manufacture, gave the product its name, "celluloid," and made it an article of commerce.

The uses of celluloid are extremely varied, and even a list is too large for the scope of this paper.[6] Suffice it to note that celluloid has entered as a material into so many fields that it is no longer considered primarily as a substitute for, or imitation of, other materials (horn, ivory, bone, tortoise shell, onyx, agate, etc.), but rather as a basic raw material which resembles these others in appearance or other properties, but is valuable chiefly because of its own properties, *i. e.*, its strength, its chemical resistance, its transparence, its brilliant colors in the opaque form, its latent plasticity, etc. Every valuable primary raw material is sooner or later imitated, and celluloid is no exception to this rule. The attempt has been made and is still being made to find a celluloid substitute. It must cost less than celluloid, retain practically all the valuable properties of celluloid and have other valuable properties of its own, while losing some of the unfavorable properties of celluloid. And let it be said at once that this search has by no means been unsuccessful. New products have been invented, some with particularly valuable properties, but all of them have only limited applications. Bakelite,[7] for instance, has come prominently into the field of plastic products, bringing with it some extremely valuable properties and making for itself a distinctive place without really competing with celluloid.

Certain disadvantageous properties of celluloid are well known to everybody.

1—It is easily inflammable.

2—It has a marked and none too pleasant odor.

3—The temperature at which celluloid becomes plastic is not far below the temperature at which the first evidence of decomposition appears.

Of course, celluloid possesses certain other properties, which may be improved. For instance, the elasticity may be improved until it approaches that of ivory, in which case celluloid could be used for billiard balls.

CELLULOID SUBSTITUTES

A long series of attempts has been made to obtain a product in place of celluloid without its disadvantages, and having the further advantage over celluloid of a lower price. In carrying out these attempts the lines of development have followed several directions:

1—Products not based on cellulose esters, such as:

(*a*) Casein derivatives;[1] (*b*) gelatin derivatives;[2] (*c*) phenol-formaldehyde condensation products;[3] (*d*) resin derivatives, etc.[4]

2—Products based on cellulose esters other than cellulose nitrate such as:

(*a*) Acetate[5] (especially "cellon"); (*b*) xanthates;[6] (*c*) mixed esters.[7]

3—Products based on cellulose nitrate but with a substance other than camphor ("camphor substitute") as the nonvolatile solvent or gelatinizing agent.

Classes 1 and 2 will be discussed in later papers and the third class only in the present paper.

CELLULOID

It will not be amiss to discuss very briefly the nitrocellulose camphor product known as celluloid.[8]

COMPOSITION—Celluloid (the common name for all pyroxylin plastics) is a solid solution of nitrocellulose and camphor (or camphor substitute) which becomes plastic on being heated. The camphor (or camphor substitute) may be considered as the solvent and the softening and plasticifying agent. The more camphor (or camphor substitute) the celluloid contains the more easily it softens and the lower is the temperature at which it becomes plastic. The higher the proportion of nitrocellulose the more elastic (in the exact, scientific sense of "elastic") is the celluloid, as well as harder and more resistant. Not every nitrocellulose yields a plastic product with camphor; only those are suitable for celluloid manufacture which are completely soluble in a 10 per cent solution of camphor in alcohol. Only a part of the camphor in celluloid can be sublimed out or driven off by heat; 10 to 15 per cent (of the weight of the celluloid) remains behind and can be removed only with difficulty, *i. e.*, by extraction with certain solvents, or by saponification of the nitrocellulose. The usual composition of celluloid is 30 to 40 parts of camphor to 100 parts of nitrocellulose. If the general formula of nitrocellulose is accepted as

---

[1] Received February 7, 1921.

[2] *Kunststoffe*, **1914**, 277; THIS JOURNAL, **6** (1914), 156, 440.

[3] Brit. Patent 1313 (1865).

[4] Brit. Patent 3102 (Oct. 1869) and U. S. Patent 97,454 (Nov. 30, 1869)

[5] THIS JOURNAL, **6** (1914), 156, 440; U. S. Patent 105,338 (July 1870).

[6] F. Sproxton, *J. Soc. Chem. Ind.*, **39** (1920), 352; J. H Stevens, "Raw Material," **1**, 227.

[7] See H. Lebach, *Chem.-Ztg.*, **37**, 733, 750.

[1] "Galalith," for instance, D. R. P. 141,309 and 147,994 (1903).

[2] For instance, L. Trommer, D. R. P. 278,667 (April 27, 1913).

[3] See C. F. Chandler's Perkin Medal Presentation Address, Award to L. H. Baekeland, THIS JOURNAL, **8** (1916), 179

[4] D. R. P. 49,507 (March 13, 1889), Wallerstein and Knoll, celluloid substitute for picture frames is made by adding a solution of borax or potash and a dye to melted white shellac, then a fibrous binding material like asbestos and a filler of lithopone or zinc white.

[5] Cellon is manufactured by the Rhein.-Westf. Sprengstoff A.-G. at Cologne and consists of cellulose acetate and camphor substitutes. It is practically noninflammable.

[6] French Patent 188,823 (January 19, 1906), Soc. Française de la Viscose.

[7] For instance, U. S. Patent 1,354,726 (Carroll) of Oct. 5, 1920, employing cellulose nitrate and cellulose acetate with tetrachloronaphthalene and triphenyl phosphate.

[8] "Celluloid" was the name applied by Hyatt to his product. Thorpe, "Dictionary of Applied Chemistry," Revised Edition **1912**, I, 705, gives brief sketch of manufacture and typical composition of celluloid.

$$C_{24}H_{40-n}-N_nO_{20+2n}$$

the nitrocellulose used for celluloid manufacture is chiefly a mixture of the hexanitrate $C_{24}H_{34}O_{20}(NO_2)_6$ (9.13 per cent N), heptanitrate $C_{24}H_{33}O_{20}(NO_2)_7$ (10.18 per cent N), and octonitrate $C_{24}H_{32}O_{20}(NO_2)_8$ (11.11 per cent N), the mixture varying from 9.5 per cent to 11 per cent in nitrogen content.

Opaque celluloid usually contains mineral matter, zinc oxide being used commonly when a white or "ivory" celluloid is desired.

PROPERTIES—The most widely accepted belief is that celluloid is a solid colloidal solution.[1] Its properties are very remarkable. It begins to soften at 80° to 90° C.[2] and can be shaped and molded at a somewhat higher temperature; the rigidity returns on cooling. It comes from the mold clean and retains its shape and appearance almost indefinitely. It may be colored very readily either by pigments or dyes, and suitable mechanical treatment can develop strength and color effects of remarkable beauty, ranging from brilliant, uniform, translucent shades to the finest effects in imitation of onyx, agate, and tortoise shell; or the product can be made transparent and almost colorless, or of opaque ivory whiteness.

DISADVANTAGES—Drawbacks to the use of celluloid have been previously mentioned, its price, inflammability, and odor. Its rather easy inflammability has prevented its use in certain limited fields, but has left its usefulness largely undiminished, as is evidenced by the fact that noninflammable substitutes have not replaced celluloid to any great extent. The odor, while unpleasant to many people, is not a serious drawback, although an odorless celluloid would undoubtedly possess certain advantages. The melting point of camphor is a more serious drawback in the manufacture of celluloid than is generally understood. Much confusion of thought exists on the subject.[3] One compiler[4] contradicts himself by considering the high melting point an advantage and then a disadvantage.

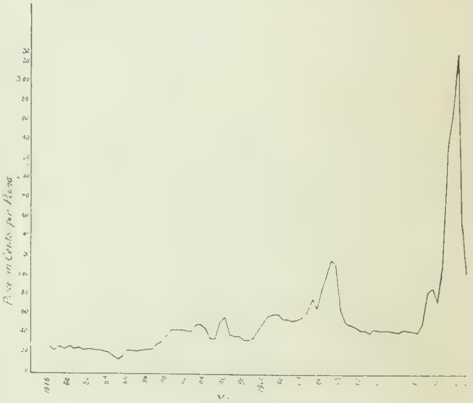
The high melting point of camphor does necessitate a high molding temperature (if a hard, low-camphor celluloid is to be manufactured), and this makes it necessary to exercise the greatest care to prevent discoloration of the ivory and transparent colorless grades of celluloid. It is most important to note that the generally recognized good qualities of camphor, its high solvent power for nitrocellulose, its comparative chemical stability, its colorlessness and freedom from poisonous effects on the workers, are the very foundations of the celluloid industry, and that any satisfactory camphor substitute must duplicate these desirable qualities.

THE PRICE OF CAMPHOR

A really serious drawback has been the controlling influence of the price of camphor. The price of camphor since 1878 (the earliest date available to the authors) on the dates specified is given in the table,[1] in cents per pound for American refined camphor in New York City:

	Jan. 1	July 1		Jan. 1	July 1
1878	0.28	0.24	1900	0.51	0.59½
1879	0.27½	0.25	1901	0.60½	0.60½
1880	0.28	0.25	1902	0.57	0.57
1881	0.26	0.23½	1903	0.54½	0.55½
1882	0.24½	0.23½	1904	0.58½	0.62
1883	0.23	0.22½	1905	0.78	0.68
1884	0.21	0.18	1906	0.88	1.00
1885	0.16	0.18	1907	1.17	1.14
1886	0.23	0.23	1908	0.68	0.52
1887	0.22	0.23	1909	0.50	0.48
1888	0.24	0.25	1910	0.45	0.45
1889	0.30	0.32	1911	0.42	0.46½
1890	0.39	0.45	1912	0.44	0.44
1891	0.45	0.45	1913	0.44	0.42½
1892	0.43	0.42	1914	0.42½	0.44½
1893	0.50	0.50	1915	0.44½	0.43
1894	0.45	0.37	1916	0.42	0.52
1895	0.36	0.53	1917	0.86½	0.89½
1896	0.59	0.40	1918	0.76½	1.11½
1897	0.39	0.39	1919	2.35	2.65
1898	0.35½	0.34½	1920	3.30	1.55
1899	0.37½	0.44½	1921	1.00	....

The accompanying graph brings out the wide fluctuations, the sudden rises and declines in the price of camphor more clearly.



CAMPHOR PRICE FLUCTUATIONS 1878–1921

THE JAPANESE CAMPHOR MONOPOLY—The successful production of synthetic camphor or the production of plantation camphor would tend to stabilize camphor prices, but the Japanese camphor monopoly has been able to prevent either form of competition from becoming strong by suitable price adjustments at the critical times, thus making it a hazardous attempt financially to go into the production of synthetic or plantation camphor. The monopoly has recently decided to refine all its camphor and to export no crude camphor. This places the celluloid industry of the world, which has already for so long labored under the disadvantage of fluctuating camphor prices, under the further danger of having its camphor supply cut off entirely whenever the Japanese celluloid industry is sufficiently advanced to warrant such a step. This opinion is confirmed by the reports that the Chinese crude camphor supply, which seemed to offer relief to celluloid manufacturers, is passing into the control of the Japanese monopoly.

CAMPHOR SUBSTITUTES

Various substitutes for camphor have been proposed and their use protected by patent grants. Many of them are obviously useless because they are more expensive even than camphor. Others are colored; some produce a celluloid which is explosive; still others liberate acid which makes the celluloid unstable, and, finally, some of the substitutes proposed have little or no solvent power for nitrocellulose. Although success to a certain extent has been attained, especially in the last two years, the list of failures has been so great that writers have been moved to say:

---

[1] H. Schwarz, *Kolloidchem. Beihefte*, **6** (1914), 90; *Z. Chem. Ind. Kolloide*, **12** (1913), 32.

[2] Plasticity has been noted at as low as 65° C. Celluloid is very plastic at 125° C. It loses color and transparency at 140° C., and begins to decompose with evolution of gas at 145° C.

[3] Auerbach, *Gummi-Ztg.*, **21** Suppl. (Jan. 25, 1906), 33, considers the high melting point of camphor an advantage.

[4] The writers too frequently ride a hobby and attempt to plead a case. Worden, "Nitrocellulose Industry," 249 (of course, W. is only quoting the literature and not giving his own opinion), in listing the advantageous properties of camphor says: "3. It has a high melting point (175°).... and therefore gives a solid celluloid, but temperature of liquefaction is not so high as to cause incipient decomposition of the celluloid." A few pages further, p. 257: "The principal objection to the use of camphor is its high melting point, which is above the decomposition point of pyroxylin. So much heat is required to mold the camphor-pyroxylin compound that there is always a tendency to discoloration and increased liability to decomposition."

[1] *Oil, Paint Drug Rep.*, 1878 to 1920.

> "Of the latter [camphor], however, we may affirm that, whatever be the camphor substitute employed, no product having all the properties and qualities of celluloid manufactured from nitrocellulose and camphor can be obtained."[1]
>
> "The feverish search for a camphor substitute has been less successful, though large classes of solid solvents of pyroxylin were discovered. A few of them, belonging to the group of acid derivatives of aromatic amines, find a limited application for special purposes."[2]
>
> "It is otherwise with camphor substitutes, which, called into life by the former high prices of camphor, played a not unimportant role for several years. They have since been avoided as they are easily prone to hydrolysis, or to oxidation, or to the liberation of acids which are detrimental to the nitrocellulose, the decomposition of which they induce or accelerate. By camphor substitute is meant a material which, though it does not possess all the properties of camphor, yet resembles it to the extent that it gives a solid solution with nitrocellulose, which softens on warming and becomes plastic, and is less inflammable than nitrocellulose. The number of such substitutes is legion. The author from his own experience has determined the worthlessness and even danger of the entire group of substitutes."[3]

RECENT SUCCESS IN MANUFACTURE—In spite of all this unfavorable evidence it is nevertheless a fact that a great measure of success has been attained with certain camphor substitutes in the United States in the last two years. One company announces in an article, "Celluloid without Camphor,"[4] the manufacture of celluloid without natural or synthetic camphor. According to this article, the new formula eliminates both odor and taste and "reduces inflammability 50 to 80 per cent." Both in the sheet or raw material form and in manufactured articles of use the appearance is the same, and the transparency is greater in the translucent form. This last statement as to increased transparency made in the above-mentioned article should be accepted with reserve.

At the Sixth National Exposition of Chemical Industries held in New York City, September 1920, there was exhibited a product which proved upon analysis to be nitrocellulose colloided by a phenol-phosphoric acid compound. The many beautiful forms in solid colors and mottlings and in imitation of various rare and expensive natural products showed the success that had been attained by the manufacturer, although further evidence as to the working qualities and resistance to external influences of these products is required before complete success can be considered as having been attained. A third company has also been successful in producing celluloid, both transparant and opaque, in which the camphor is entirely replaced by camphor substitute. Three other companies, thus including all the very largest manufacturers of celluloid in the United States, have manufactured and sold celluloid in which the camphor was partly or totally replaced by camphor substitutes, although an equal degree of success was not obtained by all of them. In all cases the product is similar to the camphor product, but there are minor differences in hardness and density, though the plasticity is approximately the same. The differences are so small that no important change is necessary at any stage of the manufacturing process, though it is to be expected that just as the various manufacturers differ even for the camphor product in the percentage of solvent, time for kneading, drying and seasoning, etc., so there will be minor changes of this nature necessitated by the introduction of a new raw material into the process.

The greatest difficulty has been that of producing "ivory." Most of the substitutes are esters, and minute traces of acids liberated from these esters, or traces of oxidation products of the substitutes have a slight action on the nitrocellulose or on the fillers used, so that occasionally a run is off-color. Proper choice of the substitute with proper conditions of colloiding and proper fillers and opacifiers will ultimately overcome this difficulty. It is to be hoped that the criticism of celluloid manufacturers of the United States uttered in 1912 is no longer true:[1]

> A long experience in this and allied industries in the United States had demonstrated that the machinery and processes hitherto employed left much to be desired in the way of improvement, of which there had been practically none during twenty years. This condition was and is due, in all probability, to the mistaken policy of manufacturers in the maintenance of secrecy, as a consequence of which inventors, manufacturers of machinery, and scientists are kept in ignorance of the necessity for the application of their knowledge and energies in the progressive improvement which is necessary to the proper development of any industry.

The camphor-celluloid industry did not spring fully developed from the ground, and research and time will be necessary to develop fully the camphor-substitute celluloid industry. Low camphor prices and an adequate supply may largely remove the incentive to the use of substitutes.

SUBSTANCES USED—There is a very marked dearth of information on the results of the use of the various camphor substitutes, and, unfortunately, the patent literature is not a reliable source of knowledge. It is known, however, that pinene hydrochloride, for instance, which does gelatinize nitrocellulose continues to liberate hydrochloric acid rather easily, "souring" the celluloid, and has thereby caused explosions of celluloid. Other chloro derivatives as well as nitro compounds are similarly dangerous. Borneol acetate, but little cheaper than camphor, has only slight solvent action and a more disagreeable odor than camphor. However, the information is generally scanty, and even then is usually colored by the inventor's claims.

The substitutes chiefly used in the United States are the phosphoric esters, triphenyl phosphate and tritolyl phosphate (often called tricresyl phosphate), triacetin, ethyl acetanilide, and other substances to a lesser degree. Triphenyl phosphate and tritolyl phosphate have been successfully used as complete or as partial camphor substitutes, the others more often as partial camphor substitutes. The essentials in all of these substances are that the product when fused or in solution in a colorless solvent shall be colorless, and that the by-products resulting from the manufacture, such as phenol, cresol, hydrochloric acid, phosphoric acid, monoacetin, acetic acid, aniline, acetanilide, etc., shall be completely removed. (That this purity is essential is indicated by British Patent 16,271 (1906), specifying as camphor substitutes *specially* purified carboxylic acid derivatives of secondary aromatic-aliphatic amines.) For instance, the impurities tenaciously retained by triphenyl phosphate are traces of acid and phenol. Yet it has been possible commercially to reduce the acidity of triphenyl phosphate to 0.001 per cent, calculated as HCl, the phenol to 0.002 per cent, and the ash content to less than 0.01 per cent. In other words, it is commercially possible to produce a camphor substitute which is more nearly a chemical individual than is commercial camphor.

---

[1] Masselon, Roberts, and Cilliard, "Celluloid," trans. by Herbert H. Hodgson, London, **1912**, 1; see also F. Sproxton, *J. Soc. Chem. Ind.*, **39** (1920), 352*r*.

[2] R. C. Schüpphaus, THIS JOURNAL, **7** (1915), 290.

[3] Ullmann, "Enzyklopaedie der technischen Chemie," III, 308.

[4] *Chem. Age* (*N. Y.*), **28** (1920), 153.

[1] Axtell, THIS JOURNAL, **5** (1913), 38.

It was thought for a time that only aromatic substances were suitable camphor substitutes, but, as the patent literature shows, numerous aliphatic substances possess solvent action toward nitrocellulose. Many of the substitutes proposed are acid derivatives of the amines or are esters, both of which classes of compounds may be fairly easily saponified or hydrolyzed, yielding acid products which accelerate the further splitting up of the compound and act deleteriously on the nitrocellulose. Others of the substitutes oxidize easily, also yielding acid products which are detrimental to the celluloid. Some of the substitutes are highly chlorinated derivatives which color easily and give off acid decomposition products.

It must be borne in mind that in order to be a satisfactory camphor substitute a substance need not necessarily be a nitrocellulose solvent. For instance, ethyl alcohol is not a nitrocellulose solvent, but if some camphor is dissolved in it (insufficient camphor to dissolve the nitrocellulose without alcohol) it becomes an excellent solvent for nitrocellulose. A case very much to the point is that of ether-alcohol mixtures. Neither ether nor alcohol alone is capable of dissolving nitrocellulose, but the mixture is a very efficient solvent. And so it is with other substances. Alone they may be ineffective, but in mixture with other solvents or non-solvents, or first dissolved in volatile solvents, these apparently nonsolvent substances may dissolve nitrocellulose, yielding a plastic product when the volatile solvent has been removed. It is a fact, however, borne out by experience with many substitutes, that those substitutes are best which, like camphor, are capable of dissolving nitrocellulose alone with the aid only of heat, pressure, and other mechanical treatment.

HARDNESS OF PRODUCT—Manufacturers of celluloid claim that the substitutes produce a soft celluloid. The softness or hardness of celluloid depends on the percentage of camphor or substitute in the celluloid. Camphor sublimes rather easily, so that camphor celluloid which is molded or otherwise heat-treated loses camphor from the surface, leaving a film of celluloid deficient in camphor and consequently hard. This "case-hardening" effect produced by the volatility of camphor is, of course, not obtained with substitutes which do not sublime at all. If a smaller percentage of the substitute is used so that the requisite hardness be obtained, difficulty is met in obtaining complete colloiding. The obvious remedy is to use less substitutes than camphor to obtain the same hardness, a larger proportion of solvent, and a longer period of kneading to produce gelatinization.

CHARACTER OF MOST DESIRABLE SUBSTITUTES—The chemical properties of camphor make it almost the ideal solvent for nitrocellulose. Camphor is a saturated cyclic ketone. This means that camphor is a relatively stable compound not oxidized by air at ordinary, or at celluloid-molding, temperatures.

The most highly desirable camphor substitutes would seem to be substances similar in structure to camphor, and, indeed, Raschig[1] protects the use of cyclohexanone, a liquid (m.p.—45° C.). The boiling point, 161° C., is perhaps too low. It is the simplest six-membered cyclic saturated ketone, but it has not come into use. Ketones of a totally different kind, such as dinaphthyl ketone,[2] have also been proposed. Substances related to camphor have been patented, as isobornyl acetate[3] and borneol.[4]

The great mass of substitutes proposed consists, however, neither of substances resembling camphor in structure, nor of substances related to camphor, but of esters, amines, and of such various substances as naphthalene, dinitrobenzene, acetodichlorohydrin, resins, starch-formaldehyde condensation products, substituted ureas, gelatin, dioxydiphenylsulfone, etc.

TRIPHENYL AND TRITOLYL PHOSPHATE CELLULOIDS

As indicated above, of all this imposing array of substitutes only a few have attained any success at all, and of these only triphenyl phosphate and tritolyl phosphate have been very successful in the United States. It is claimed for celluloid made with phenol esters of phosphoric acid that it is superior to camphor celluloid in these respects:

1—It is less inflammable.
2—It is absolutely odorless.
3—It is very resistant to all external influences.
4—It is cheaper.

Triphenyl phosphate is a low-melting, white solid (resolidification point 49.9° C.). Tritolyl phosphate (tri-*o*-tolyl phosphate) is a viscous liquid which becomes very thick and glassy at—30° C. but does not solidify. In the liquid state both substances are colorless when pure. They are without odor or taste, nonvolatile, boil at very high temperatures, are stable towards air and water, and do not color on exposure to light if they have been properly purified. They saponify with difficulty, and in their solvent action on nitrocellulose they resemble camphor. Some workers[1] who have examined plastics of different makes containing triphenyl and tritolyl phosphates have found instances of brittleness, which they explain as due to insufficient colloiding power of these substances on nitrocellulose. The authors' experience is that the colloiding power of the above phosphates is approximately equal to that of camphor, but that more careful and longer continued mechanical treatment (in kneaders, on rolls, etc.) is necessary to bring out the full colloiding action of triphenyl and tritolyl phosphates. The difficulties arising from the use of these substances as camphor substitutes have already been discussed, but the overcoming of these difficulties to a certain extent is amply evidenced by their widespread use when camphor prices rose. Their use is determined to a large measure by the price of camphor, but this is not the only factor. The camphor must be used with volatile solvents to overcome the difficulty arising from its high melting point. For the effective use of these solvents, chiefly alcohol, the nitrocellulose must be dehydrated. Alcohol would mix with the water contained in wet nitrocellulose, and the diluted alcohol is a poor solvent. Part of the volatile solvent is lost; usually none is recovered, or only at great cost. The liquid condition of tritolyl phosphate and the low melting point of triphenyl phosphate permit the use of these substitutes in the liquid condition without a solvent or with small proportions of solvent and wet nitrocellulose. These liquids are immiscible with water and displace the water from the nitrocellulose as they colloid it.[2] The water can then be removed in any convenient way. Furthermore, by proper choice of the camphor substitute or mixtures, a celluloid of the proper solidity can be produced which can be molded at a lower temperature than camphor celluloid.

TRIACETIN AND ETHYL ACETANILIDE

Triacetin has been used to a certain extent to replace part of the camphor of celluloid. Some manufacturers have experienced a fair degree of success with this substitute, while others have claimed that it causes blistering of the celluloid and liberates acid. It may be that some of the defects which have been found in triacetin, as in other camphor substitutes, are due to insufficient purification.

---

[1] U. S. Patent 900,204.
[2] Zühl and Eisemann, D. R. P. 122,166 (Oct. 28, 1900).
[3] Claessen, D. R. P. 172,941 (April 7, 1905).
[4] Béhal, U. S. Patent 831,028.

[1] Private communication.
[2] Lindsay, U. S. Patent 1,233,374 (July 17, 1917).

Ethyl acetanilide, or mannol, has also been used in the United States, but it is not very satisfactory. It produces a soft celluloid, which hardens on aging but becomes brittle. The higher cost, odor, and discoloration in sunlight are serious objections.

PATENTS COVERING CAMPHOR SUBSTITUTES

Following is a list of the patents for camphor substitutes. Most of them have evidently no value and others which may have value have never been used commercially, but all are included for the sake of completeness.

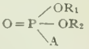
NUMBER	PATENTEE	DATE	CONTENT
			U. S. Patents
269340	Stevens	Dec. 19, 1882	Certain essential oils, esters and ethers
269341	Stevens	Dec. 19, 1882	Oil of caraway seed, hyssop, sage, tansy, cloves or wintergreen
269342	Stevens	Dec. 19, 1882	Dinitrobenzene, coumarin
269345	Stevens	Dec. 19, 1882	Fusel oil plus oil of hyssop, sage, tansy, wormseed, fennel seed, cloves, anise, cinnamon, sassafras, camomile, wintergreen, caraway seed, dill, acetal, amyl nitrate and amyl nitrite
366231	McClelland	July 12, 1887	Nonvolatile gums and resins, such as kauri gum, dammara resin, and gum dammar
410205	Schüpphaus	Sept. 3, 1889	Anthraquinone
410206	Schüpphaus	Sept. 3, 1889	Isovaleric aldehyde or its derivatives, amylidene dimethylether, amylidene diethylether
410207	Schüpphaus	Sept. 3, 1889	α-Naphthol and β-naphthol
410208	Schüpphaus	Sept. 3, 1889	Mixture of acetins
410209	Schüpphaus	Sept. 3, 1889	Palmitin and stearone
494790 494791 494792 494793	Paget	Apr 4, 1893	Distillate from sulfuric acid and two or more primary alcohols, distillate treated with an acid which will combine with the ethers or esters so formed and redistilled. Redistillate is the subject of patent
500617	Stevens and Axtell	Dec. 12, 1893	Acetanilide
517987	Stevens	Apr. 10, 1894	Acetanilide
528812	Schüpphaus	Nov. 6, 1894	Acid derivatives of aromatic amines, one H in NH_2 replaced by acid
542692	Stevens	July 16, 1895	Dinitrotoluene
543108	Stevens	July 23, 1895	Dinitrotoluene
543197	Stevens	July 23, 1895	Naphthalene (partial replacement)
551456	Stevens	Dec. 17, 1895	Methyl, ethyl, propyl, butyl, and amyl acetanilides
552209	Stevens	June 12, 1895	*p*-Nitrotoluene
552934	Stevens	Jan. 14, 1896	Camphene hydrochloride
553270	Stevens	Jan. 21, 1896	Dinitroxylene
559823	Stevens	May 12, 1896	Product of oxidation of mixture of alcohols
559824	Stevens	May 12, 1896	Mixed benzoic esters
561624	Stevens	June 9, 1896	Mixed formic esters
564343	Stevens	July 21, 1896	Acetoxylidide
566349	Stevens	July 26, 1895	Antipyrine, tolypyrine, salipyrine, and tolysal
568104	Stevens and Axtell	Sept. 22, 1896	Carbanilates containing radicals of the monohydric monatomic fatty alcohols
568105	Stevens	Sept. 22, 1896	Citric esters of monohydric monatomic fatty alcohols and chloro and acetyl derivatives of these citric esters
568106	Stevens	Sept. 22, 1896	Urethanes or carbamates of the monohydric monatomic fatty alcohols, also benzyl carbamates, ethylidene urethane, acetyl-*p*-oxyphenylurethane and acetyl-*p*-ethoxy-phenylurethane
572134	Stevens	Dec. 1, 1896	Certain derivatives of crystalline aromatic acids, salol, betol or naphthalol, benzonaphthol, salacetol and benzoic anhydride
572135	Stevens	Dec. 1, 1896	Crystalline organic sulfur compounds such as trional or diethylsulfonemethylethylmethane, sulfobenzide or diphenylsulfone, sulfonal or diethylsulfonedimethylmethane, and sulfocarbanilide or *s*-diphenylthiocarbamide
583516	Stevens	June 1, 1897	Crystalline halogen derivatives, and nitrohalogen derivatives of benzene, toluene, naphthalene, camphor, and phenol
583517	Stevens	June 1, 1897	Crystalline nitro derivatives of naphthalene and phenol
587096	Kennedy	July 27, 1897	Lanolin
595355	Stevens	Dec. 14, 1897	Aliphatic ketones, both symmetrical and unsymmetrical
596662	Nagel	Feb. 3, 1896	"Hydrochlorinated turpentine" or "camphene" (pinene hydrochloride)
597144	Goetter	July 22, 1896	Amyl acetate
598648	Schüpphaus	Feb. 8, 1898	Monobenzoate of glycerol, benzochlorohydrin, dichlorohydrin, dichloroacetin, benzomonoacetin, benzodiacetin, oleoacetin, oleodiacetin, dinitroacetin, mononitrodiacetin
598649	Schüpphaus	Feb. 8, 1898	Acetophenone, benzylidineacetone, benzophenone, phenylbenzylketone, oxyacetophenone, benzil, dibenzylidineacetone, trioxybenzophenone, *p*-oxybenzophenone, oxyphenylbenzylketone, trioxyacetophenone
604181	Walker	May 17, 1898	Oils lighter than water obtained by the distillation of the tar of hardwoods
607554	Stevens	July 19, 1898	Certain crystalline derivatives of phenols or aromatic alcohols, dimethylhydroquinol, thymoquinone, thymol and benzoylguaiacol
700471	Bernadac	May 20, 1902	Casein (alone or made plastic by borax)
700884	Zuhl	May 27, 1902	Diphenyl carbonate, dicresyl carbonate and dinaphthyl carbonate
700885	Zuhl	May 27, 1902	Triphenyl phosphate, tricresyl phosphate, trinaphthyl phosphate
741554	Schüpphaus	Oct. 13, 1903	Mixed ethers of the lower alcohols
758335	Schmidt	Apr. 26, 1904	Compounds of general formula $R\text{-}SO_2A$, where R means an aromatic radical or its substitution product. $R\text{-}SO_2A$ is the sulfonic derivative thereof, in which OH has been replaced by A, an aliphatic or aromatic ether residue
831028	Béhal	Sept. 18, 1906	Borneol or isoborneol
831488	Thieme	Sept. 18, 1906	Ureas in which hydrogen associated with nitrogen is substituted by organic radicals
881827	Rouxeville	Mar. 10, 1908	Polymerized oil of turpentine
892899	Schraube and Laudien	July 7, 1908	Amidines derived from *o*-diamines, especially from *as*-trichlorodiaminobenzene and *v*-tetrachlorodiaminobenzene
900204	Raschig	Oct. 6, 1908	Cyclohexanone
946294	Vender	Jan. 11, 1910	Water-soluble acetins
961360	Lindsay	June 14, 1910	Benzyl benzoate
962877	Aylsworth	June 28, 1910	Halogenated fatty acids and their esters
996191	Ach	June 27, 1911	Organic cyclic oxides (oxygen, one or preferably more atoms in ring attached to two carbon atoms, which latter are not attached to oxygen outside of the ring), which may be produced by condensing aldehydes or ketones with polyhydric alcohols
1027617	Lindsay	May 28, 1912	Ethylene chlorohydrin
1027618	Lindsay	May 28, 1912	Ethylene acetochlorohydrin
1082573	Weedon	Dec. 30, 1913	Aldehyde-alcohols, especially acetaldol
1152625	Goldsmith	Sept. 7, 1915	Oils (drying and nondrying), oxidized by dilute nitric acid

Number	Patentee	Date	Content
1158961	Beatty	Nov. 2, 1915	Dioxydiphenyldimethylmethane
1188356	Beatty	June 29, 1916	Dioxydiphenyldimethylmethane
1191801	Lehmann and Stocker	July 18, 1916	Polymers of cumarone and indene
1195040	Lederer	Aug. 15, 1916	Chloral hydrate
1200886	Schmidt	Oct. 10, 1916	Acyl compounds of completely hydrogenated amines
1309981	Clarke	July 15, 1919	Simple higher dialkyl oxalates
1354725	Carroll	Oct. 5, 1920	Mixture of tetrachloronaphthalene and triphenyl phosphate
1360759	Kessler	Nov. 30, 1920	Acetins free from monacetin and free acetic acid
			German Patents
56946	Güttler	Dec. 17, 1889	Nitrocarbohydrates (cellulose, sugar, starch, gums) are fused with solid derivatives of the hydrocarbons (dinitrobenzene and dinitrophenol)
66055	Koller	Mar. 29, 1892	A paste of nitrocellulose, sulfur, nondrying oils, and resins or their solutions in oils is heated with viscous collodion at 100°–105° in an autoclave at 12 atmospheres pressure
80776	Schüpphaus	Nov. 6, 1894	Formanilide, *o*-acetophenetidine, *o*-acetotoluidide, *p*-acetophenetidine, *p*-acetotoluidide, benzanilide, and their bromo and nitro derivatives
85235	Marga	Sept. 5, 1894	Pure cellulose or mechanical wood powder is added to an alcohol-ether solution of nitrocellulose (Celludine)
96365	Beid and Earle	Nov. 28, 1895	Nitro derivatives of oils containing linolein or ricinolein are mixed with nitrocellulose
102962	Stracke	Sept. 2, 1898	Resin soaps and finely divided resin- or bitumen-containing substances (bark, rich peat, and bituminous shales) are mixed with nitrocellulose and pressed hot
114278	Kohl	July 19, 1899	Pyroxylin and gelatin in glacial acetic acid
115681	Spitaler	July 15, 1899	Albuminoids, especially casein, freed from constituents insoluble in caustic, are dissolved in borax and distilled water, and gelatinized paste added to nitrocellulose
117542	Société Générale pour la Fabrication des Matières Plastiques	June 28, 1899	Naphthalene
118052	Zühl and Eisemann	Apr. 15, 1900	α-Naphthyl acetate or β-naphthyl acetate is treated with twice its weight of nitrocellulose in the presence of solvents (methanol)
119636	Zühl and Eisemann	July 7, 1900	Phenoxylacetic acids, naphthoxylacetic acids or their anhydrides or esters are treated with nitrocellulose
122166	Zühl and Eisemann	Oct. 28, 1900	Methylnaphthylketone, dinaphthylketone, methoxynaphthylketone or dioxynaphthylketone is treated with nitrocellulose in the usual manner
122272	Höchst	Oct. 10, 1900	Aromatic sulfonic acid derivatives which are derived from chlorides, esters, and amides; especially *p*-toluenesulfoalkyl- and -dialkylamides and other derivatives obtained in the preparation of saccharin from *p*-toluenesulfonechloride, such as *p*-toluenesulfonic acid alkyl ester, *p*-toluenesulfonic acid alphyl ester, *p*-toluenesulfamide. For this purpose there are always used two or more bodies of the groups named
125315	Goldsmith and British Xylonite Co., Ltd.	Oct. 31, 1900	Reaction products of hydrochloric acid solution (or gas) and acetic acid and glycerol, such as acetodichlorohydrin, diacetochlorohydrin, monoacetomonochlorohydrin, which are used alone or in mixture; for instance, to 100 parts of soluble nitrocotton, 5 parts of camphor and 20 parts of the above-named substitutes in alcoholic solution are added
127816	Höchst	June 30, 1900	Neutral alkyl or alphyl esters of phthalic acid
128119	Zühl and Eisemann	Mar. 10, 1901	Nitrocellulose is treated with oxanilic acid esters in which the aniline may also be replaced by homologous or substituted bases of the aromatic series
128120	Zühl and Eisemann	Mar. 21, 1901	To nitrocellulose are added phenol esters of phosphoric acid, such as triphenyl phosphate, tricresyl phosphate, trinaphthyl phosphate
128956	Zühl and Eisemann	Mar. 21, 1901	Mono- or polyhalogen substitution products of aromatic hydrocarbons, such as dichlorobenzene and monochloronaphthalene
132371	Deutsche Zelluloidfabrik	May 15, 1901	Acetyl derivatives of such secondary amines as have two hydrogen atoms of the ammonia replaced by aromatic radicals, such as acetyldiphenylamine
138783	Franquet	July 25, 1901	Casein made plastic by borax solution and then dehydrated is added to a solution of nitrocellulose
139589	Zühl and Eisemann	Sept. 30, 1900	Phenol esters of carbonic acid such as diphenyl carbonate, dicresyl carbonate, or dinaphthyl carbonate
139738	Goldsmith and British Xylonite Co., Ltd.	Dec. 14, 1901	One or more acid or neutral esters of sebacic acid; for instance, 100 parts nitrocellulose are worked up in alcoholic solution with 40 parts of the finally purified product obtained by the oxidation of castor or coconut oil by nitric acid and subsequent esterification with methanol
139905	Franquet	Feb. 23, 1902	In No. 138783 casein is replaced by caseinates
140164	Zühl and Eisemann	Oct. 27, 1901	Triphenyl, tricresyl, and trinaphthyl thiophosphates
140263	Rheinische Gummi- und Zelluloidfabrik	Jan. 14, 1902	Organic acid esters of the sugars (glucose, levulose and sucrose) such as acetochlorohydrose, glucose dibutyrate, glucose distearate, glucose ditartrate, glucose tetratartrate, glucose diacetate, glucose tetra-acetate, glucose penta-acetate, octacetyl glucose, penta-acetyl levulose, tetra-acetyl lactic acid, lactose tartrate sucrose mono-, tetra-, hepta- and octacetate
140480	Rheinische Gummi- und Zelluloidfabrik	Feb. 26, 1902	α- and β-Phenylnaphthalene, α- and β-dinaphthylmethane, and α-and β-benzylnaphthalene
140855	Rheinische Gummi- und Zelluloidfabrik	Jan. 14, 1902	Glucose, levulose, and lactose replace camphor, and sufficient pressure is applied to cause solution of the nitrocellulose
142452	Zühl and Eisemann	Nov. 21, 1901	Alcohol esters of phenol phosphoric acids and halogen derivatives thereof
142971	Zühl and Eisemann	May 18, 1902	Such esters as contain alcoholic groups as well as phenolic groups, such as ethyl ester of diphenyl phosphoric acid, dimethyl ester of cresyl phosphoric acid, or amyl ester of dinaphthyl phosphoric acid
142832	Zühl and Eisemann	June 16, 1902	Halogenated phenol esters of phosphoric acid, as neutral phosphoric acid esters of dichlorophenol, dichloronaphthol and tetrachloronaphthol
144648	Zühl and Eisemann	Oct. 26, 1902	Phosphoric acid derivatives in which one or two hydroxyls are replaced by phenoxy, cresoxy, or naphthoxy groups, and the remaining hydroxyls by aniline groups, such as diphenyl phosphoric acid anilide, cresyl phosphoric acid anilide or dinaphthyl phosphoric acid anilide
163668	Claessen	June 8, 1904	Low melting resins or ceresin are used with nitrocellulose completely soluble in 96 per cent alcohol; for example, 100 parts nitrocellulose are dissolved in 30 parts colophony and 60 parts 96 per cent alcohol
168497	Rheinische Gummi- und Zelluloidfabrik	July 22, 1903	Sugary or starchy products, especially dextrin, are treated with aldehydes and used as camphor substitutes, such as sugar formalin or starch formalin
172941	Claessen	Apr. 7, 1905	Isobornyl acetate
172966	Claessen	June 22, 1904	Benzylidine acetoacetic ester, or benzylidene diacetoacetic ester in mixture with each other
172967	Claessen	July 2, 1904	The above-named acetates in mixture with product obtained by the action of HCl on these substances, 3-methyl-5-phenyl-4,6-dicarboxethyl-d_2-keto-R-hexene
173020	Bad. Anil. Soda Fab.	Dec. 16, 1904	Benzylidine diacetate or its monochloro substitution products
173796	Zuhl and Eisemann	Sept. 22, 1905	Phosphoric acid esters of dichlorohydrin
174259	Claessen	Oct. 29, 1904	Nitrocellulose is dissolved in ethylidine diacetoacetic ester or in the mixture of it with benzylidine acetoacetic esters

NUMBER	PATENTEE	DATE	CONTENT
174914	Raschig	July 16, 1905	Cyclohexanone, cyclohexanol, as well as their homologs, alone or in mixture
176474	Bad. Anil. Soda Fab.	July 26, 1905	Alkylaceto compounds of tri- and more highly chlorinated anilines in which both *o*-positions to the amino group are occupied by chlorine, with the exception of *s*-methylacetotetrachloroanilide and benzylacetopentachloroanilide
177778	Zuhl and Eisemann	Nov. 18, 1904	Together with the camphor substitutes in D. R. P. 128956 and 139589 there should be added as "hardening" material such substances as resins or resinous bodies; for example, shellac, dammar, mastic, acaroid resin, colophony, resin-acid esters; for many purposes also hard resins such as copal and amber
178133	Claessen	Mar. 11, 1906	Substitution products of urea in which all the hydrogen bound to nitrogen is replaced by organic radicals
180126	Bad. Anil. Soda Fab.	Apr. 21, 1906	Amidines derived from *o*-diamines
180208	Bad. Anil. Soda Fab.	Aug. 9, 1905	*s*-Methylbenzoyltrichloroanilide
191454	Claessen	Aug. 23, 1906	Ureas or thioureas in which all the hydrogen atoms are replaced by organic radicals or their halogen derivatives
185808	Basler & Co.	June 7, 1905	Borneol or isoborneol alone or with admixture of some camphor in the presence of a solvent (ethyl acetate, amyl acetate, acetone) which is later removed
188822	Rheinische Gummi- und Zelluloidfabrik	Nov. 9, 1905	Condensation products, which result from the action of formaldehyde on terpenes, terpene-containing ethereal oils, resins, and balsams
202720	Szelinski	Dec. 28, 1907	The products of the action of organomagnesium compounds on hydroaromatic ketones such as carvone, pulegone, and cyclohexenone
207869	Desvaux and Allaire	Apr. 17, 1908	Camphor is partly replaced by the albuminoid substance obtained from maize according to D. R. P. 144217
214193	Herstein	Nov. 23, 1907	Nitrocellulose treated with caustic alkali and hardened by weak acids and salts
214398	Buchstab	July 23, 1908	Pass air through nitrocellulose solution, then add lactic acid and strontium chloride and castor oil
214962	Boehringer and Sons	Dec. 5, 1906	Cyclic ethers which are prepared by condensation on one hand from aldehydes and ketones, and on the other hand from polyatomic alcohols of the formula $CH_2OH(CHOH)_xCH_2OH$
219918	Chemische Fabrik Griesheim-Elektron	July 9, 1908	Dioxydiphenylsulfone
220228	Lederer	Feb. 24, 1907	Chloral hydrate, chloral alcoholate, etc.
221081	Soc. Indust. de Celluloid	Jan. 13, 1909	Maltodextrin neutralized with borax added to nitrocellulose-camphor (or camphor-substitute) mixtures
242467	Berend	July 16, 1908	Nitrocellulose dissolved with anhydroformaldehyde compounds of resin, oil or fatty acids and primary amines in acetone, the solution emulsified with gelatin, casein, or albumin solution, and the emulsion hardened by formaldehyde
240046	Danzer	June 23, 1910	Nitrated cellulose sheets treated with solvent for nitrocellulose
251372	Celluloid Co.	June 7, 1910	Benzyl benzoate in the presence of solvents
281225	Bad. Anil. Soda Fab.	Nov. 29, 1913	Acyl derivatives of completely hydrogenated aromatic amines (acetyldicyclohexylamine obtained by acetylation of dicyclohexylamine)
292951	du Pont de Nemours	Oct. 10, 1912	Aldehyde-alcohols, like acetaldol
319723	Clouth	Dec. 6, 1917	Cellulose esters either alone or with "softening" materials soluble in anthracene oil are mixed with anthracene oil

French Patents

NUMBER	PATENTEE	DATE	CONTENT
254695	Nagel	Mar. 12, 1896	Pinene hydrochloride or "camphene"
292983	Société Génerale pour la Fabrication des Matières Plastiques	Oct. 2, 1899	Naphthalene
295592	Cie. Paris de Couleurs d'Anilin	Dec. 23, 1899	Alphyl ethers of aromatic sulfonic acids, especially of *p*-toluenesulfonic acid, *p*-toluenesulfamide and *p*-toluenedialkylamide
300676	Marx and Destaux	May 26, 1900	Nitronaphthalene
308372	Zuhl	Feb. 22, 1901	Phthalic acid, *o*-phthalic anhydride, phthalonic acid, benzene tricarboxylic acid, and their esters
309962 Addition 148 of Feb. 22, 1902 to 309962	Zuhl	Apr. 15, 1901	Triphenyl, tricresyl, trinaphthyl phosphates; substituted products of triphenyl, tricresyl, and trinaphthyl phosphates, substituted in rings or with oxygen of $=P=O$ replaced by sulfur
312817	Franquet	July 18, 1901	Acetyldiphenylamine, triphenyl phosphate, amylidine dimethyl and diethyl esters
319926	Soc. Ind. de Cellulose	Nov. 27, 1902	Gelatin or an ammoniacal solution of gelatin
320133	Soc. Anon. l'Oyonnaxienne	Apr. 2, 1902	Camphor partly replaced by gelatin and the product hardened by formaldehyde
322506	Callenberg	June 27, 1902	Halogenated ethereal oils, especially chlorinated turpentine
331819	Soc. Anon. l'Oyonnaxienne	Oct. 3, 1903	Camphor partly replaced by albumin; hardened by formaldehyde
339081	Proveux	Oct. 5, 1903	Nitrocellulose plus camphor and casein or casein alone combined with glycerol and boric acid (Caséilithe)
340266	Schmerber	Feb. 8, 1904	Methylacetanilide
341556	Weiler-ter-Meer	Mar. 23, 1904	Mono- and polyhalogen derivatives of primary amines; acyl derivatives of halogenated primary amines and acyl derivatives of secondary aromatic-aliphatic amines
349970	Béhal, Magnier and Tissier	June 7, 1904	Borneols
352853	Gillet	Mar. 30, 1905	20–50 per cent camphor replaced by rosin or other resin of equal solubility in alcohol
362090	Claessen	Feb. 8, 1906	Benzylidine diacetylacetic ester and benzylidine acetylacetic ester
363846	Bad. Anil. Soda Fab.	Mar. 5, 1906	Alkyl-acyl derivatives of polychloroanilines containing three or more chlorine atoms, two of which are ortho to the amino group
364604	Claessen	Mar. 26, 1906	Ureas with the four hydrogen atoms attached to nitrogen replaced by organic radicals
365297	Bad. Anil. Soda Fab.	Apr. 14, 1906	Acyl derivatives of monoalkylanilines thrice or more halogenated in which two positions ortho to the amino group are occupied by halogen
366106	Bad. Anil. Soda Fab.	May 11, 1906	Amidines derived from aromatic *o*-diamines; amidines containing two atoms of chlorine ortho to the nitrogen atoms
372018	Mestrallet-Petry	Dec. 1, 1906	Gelatin
372512	Arbez-Carme	Dec. 14, 1906	Mixture of rosin and naphthalene
372599	Bondet	Dec. 15, 1906	Gelatin, glucose, resinous matters, and vegetable oil added to celluloid to make a plastic product
374395	Peyrusson	Apr. 14, 1906	Ricinates or ricinoleates of metals, especially Mg, Zn, Pb, Al, with or without chlorides of Zn, Mg, Mn, or Cu
Addition 8760 to 374395	Peyrusson	Apr. 13, 1907	Sulforicinates are equivalent to ricinates of original patent
376269	Rouxeville	June 5, 1906	Certain hydrocarbons prepared according to French Patent 356916 of Aug. 7, 1905
377010	Lederer	Apr. 20, 1907	Chloral hydrate; chloral alcoholate
377671	Weiler-ter-Meer	July 17, 1906	Acyl derivatives of secondary aliphatic aromatic amines, specially purified
382270	Gillet	Dec. 3, 1906	Rosin and castor oil
382350	Gillet	Dec. 5, 1906	Rosin and castor oil varied according to hardness desired
383478	Dubosc	June 9, 1908	Borneol esters

NUMBER	PATENTEE	DATE	CONTENT
387179	Soc. Anon. Nouvelle "L'Oyonnithe"	Feb. 12, 1908	Aliphatic esters of fatty acids derived from fats, such as palmitic, stearic, oleic, ricinoleic and linoleic
387537	Assadas	May 8, 1907	Noninflammable plastic of nitrocellulose using hypophosphorous acid or its barium salt, neutralizing free acidity by means of specified sulfur compounds, and replacing camphor by colophony
404028	Commercial Products Co.	April 14, 1909	Gelatin with or without casein and albumin in phenol or anhydrous glycerol is treated with paraformaldehyde in anhydrous glycerol, added to nitrocellulose colloided by anhydroformaldehydeaniline or the resinate of the latter
409557	Bretaeau and Leroux	Feb. 19, 1909	Aromatic aldehydes and similar alkylated or acylated derivatives; hydroaromatic ketones such as hexahydrobenzylketone, hydronaphthylketones
432264	Dreyfus	July 15, 1911	(*a*) Mono- or polyhalogenated derivatives of benzene, toluene, and naphthalene and side-chain derivatives, halogenated in lateral chain or nucleus, or both (*b*) Nitro derivatives of benzene, toluene, and naphthalene (*c*) Ethers of mono- or polyphenols (*d*) Halogenated camphor (*e*) Ketones (*f*) Side-chain aromatic alcohols (*g*) Mixtures of above
Addition 16854 to 432264	Dreyfus	Nov. 19, 1912	Instead of substances named in principal patent, products obtained by the action of metal phenolates or alcoholates on chlorinated aliphatic compounds
447645	Beatty	Aug. 26, 1912	*s*-Dihydroxydiphenyldimethylmethane and amyl acetate
449606	du Pont de Nemours	Oct. 19, 1912	Aldols, preferably nonvolatile and polymerizable, such as acetaldol
449607	du Pont de Nemours	Oct. 19, 1912	Acetaldol
452432	LeCamphre	Mar. 6, 1912	Halogen derivatives of camphor
465345	Nouvelle L'Oyonnithe	Nov. 26,1913	To nitrocellulose and camphor add 50 to 70 per cent of castor oil; the castor oil can be partially replaced by acetin or mannol For triformin, epiformin, etc., see G. Moyer, *Caoutchouc gutta-percha*, **10** (1913), 7366 For amyl and butyl ricinoleates and tartrates, see Djeinem, *Caoutchouc gutta-percha*, **17** (1920), 10402 For alkyl esters of higher fatty acids (like ethyl ricinoleate), see Luttringer, *Bull. Soc. Ind. Rouen*, **48** (1920), 81'
			British Patents
7277	Paget	Apr. 8, 1893	Mixed ethers, such as ethylamyl ether
7784	Paget	Apr. 17, 1893	Distillate from sulfuric acid and two or more primary alcohols, distillate treated with an acid which will combine with the ethers or esters so formed and redistilled. Redistillate is the subject of patent
22137	Paget	Nov. 18, 1893	Various ozonized solvents
21331	Schüpphaus	Nov. 6, 1894	Alkyl derivatives of aromatic amines and their substitution products
13287	Chaubet	June 27, 1899	Naphthalene
15355	Höchst	July 26, 1899	1.8 parts nitrocellulose dissolved in 16 parts glacial acetic acid, with 5 parts gelatin added
25434	Höchst	Dec. 22, 1899	Compounds of general formula $R-SO_2A$, where R means an aromatic radical or its substitution product. $R-SO_2A$ is the sulfonic derivative thereof in which OH has been replaced by A, an aliphatic or aromatic ether residue
13131	Goldsmith and British Xylonite Co.	July 20, 1900	Acetochlorohydrins, acetins, benzicin, esters of phthalic acid and anhydride, and esters of succinic acid, pulegone, thujone, or oils containing these, and condensation products of acetone or acetone oils with benzaldehyde, acetaldehyde, or formaldehyde
17948	Zuhl	Oct. 9, 1900	Esters of phenols or derivatives with mono- or polybasic aliphatic acids, as diphenyl carbonate, naphthol propionate, resorcinol diacetate, and others
20733	Zuhl	Nov. 16, 1900	Solid ketones such as methylnaphthylketone, dinaphthylketone, methyloxynaphthylketone, dioxydinaphthylketone
4326	Zühl	Feb. 28, 1901	Esters and anhydrides of phthalic and phthalonic acids
8063	Bonnaud	Apr. 19, 1901	Nitrocellulose in alcohol and camphor. Add gum copal in boiling castor oil, and mineral matters
8072	Zühl	Apr. 19, 1901	Phosphoric esters of phenols, and naphthols
10213	Zuhl	May 16, 1901	Halogen derivatives such as trichlorobenzene, dichloronaphthalene, trichloronitronaphthalene, trichloroaniline
22662	Goldsmith and British Xylonite Co	Nov. 9, 1901	Alkyl esters of acids obtained by oxidizing fats and soaps, including alkyl esters of oxalic acid series. Acetylated and benzoylated secondary aromatic amines. Alkyl esters of lactic and tartaric acids and their acetyl and benzoyl derivatives
9416	Edeleanu and Filiti	Apr. 23, 1902	Nitrated petroleum products
4383	Zühl	Feb. 20, 1902	Substituted products of triphenyl, tricresyl, and trinaphthyl phosphates, substituted in the rings, or with oxygen of $\equiv P=O$ replaced by sulfur
23445	Zühl	Oct. 27, 1902	Phosphoric acid derivatives of the type  $O=P(OR_1)(OR_2)(A)$ where OR_1 and OR_2 are phenoxy, cresoxy, or naphthoxy residues, and A represents an ester or anilide group
3045	Ensminger	Feb. 9, 1903	Nitrocellulose, casein and camphor plastic is decamphorated and hardened by formaldehyde
23752	Casein Co. of America	Nov. 2, 1903	Add casein dissolved in glacial acetic acid to nitrocellulose
5280	Ortmann	Mar. 3, 1904	Ketones such as methylethyl, methylnaphthyl, dinaphthyl, methoxynaphthyl, dioxynaphthyl, together with turpentine and naphthalene
9277	Woodward	Apr. 22, 1904	Noninflammable celluloid produced by mixing fish glue, gum arabic, gelatin, and rape oil with celluloid
15435	Weiler-ter-Meer	July 11, 1904	Mono- or polyhalogen derivatives of primary amines and their acyl compounds. Acid derivatives of secondary amines which contain an aromatic or aliphatic radical
11512	Béhal	June 1, 1905	Borneol and isoborneol
2817	Weiler-ter-Meer	Feb. 5, 1906 (void)	Acyl derivatives of secondary aromatic-aliphatic amines, specially purified
8077	Bad. Anil. Soda Fab.	Apr. 3, 1906	Alkyl-acyl derivatives of polychloroanilines, containing three or more chlorine atoms, two of which are ortho to the amino group
10228	Bad. Anil. Soda Fab.	May 1, 1906	Polychloroamidines and alkyl derivatives thereof (from *as*-trichlorodiaminobenzene and *v*-tetrachlorodiaminobenzene)
10228A	Bad. Anil. Soda Fab.	May 1, 1906	Amidines from *o*-diamines, and especially those produced in 10228
16271	Weiler-ter-Meer	July 18, 1906	Specially purified carboxylic acid derivatives of secondary aromatic-aliphatic amines
20037	Claessen	Sept. 8, 1906	Ureas in which the four hydrogens of the ammonia residues are substituted by organic radicals
9537	Lederer	Apr. 24, 1907	Chloral hydrate and chloral alcoholate
11397	Bethisy, Fouchard and Vignes	May 15, 1907	Bleached tetranitrocellulose with 40 to 45 per cent water content is saturated with 5 per cent liquid hydrocarbon and then treated with mixture of acetic acid, sulfuric ether, acetone, amyl acetate, and solution of *unona selanica*
21880	Self-Developing Plate Co. and Bolas	Oct. 3, 1907	Gelatinizing nitrocellulose sheet without camphor, but merely with alcohol and pressure without dissolving nitrocellulose

NUMBER	PATENTEE	DATE	CONTENT
8542	Briailles	Apr. 16, 1908	Gelatin and nitrocellulose, oil of acetone, and vaseline oil as celluloid substitute
15855	Griesheim-Elektron	July 7, 1909	Dioxydiphenylsulfone
20975	Dreyfus	Sept. 22, 1911	1—Alcoholic or phenolic ethers of mono- or polyphenols and their homologs 2—Aromatic side-chain alcohols and their substitution products
3869	Bad. Anil. Soda Fab.	Feb. 15, 1912 (void)	Lower fatty acid esters of cyclohexanol, cyclopentanol, and their homologs
18822	Beatty	Aug. 16, 1912	Dioxydiphenyldimethylmethane
22623	du Pont de Nemours	Oct. 4, 1912	(Nitrostarch or nitrocellulose), monomolecular aldols such as acetaldol
18499	Beatty	June 19, 1913	Dioxydiphenyldimethylmethane
9270	Bad. Anil. Soda Fab.	Apr. 14, 1914	Acyl derivatives of completely hydrogenated aromatic bases

The Catalytic Oxidation of Petroleum Oils[1,2]

By C. E. Waters

BUREAU OF STANDARDS, WASHINGTON, D. C.

Earlier papers from this Bureau have dealt with the oxidation of petroleum oils, chiefly in connection with a so-called carbonization test for automobile lubricating oils.[3] The idea upon which the test is based is the partial oxidation of the oil, followed by polymerization of the oxidation products to asphaltic matter.

Many oil chemists do not accept this idea, but think that the so-called carbon deposits in the engine are the result of cracking of the lubricant.[4] Be that as it may, there is no doubt that petroleum oils are rather easily oxidizable under certain conditions and yield precipitates when diluted with petroleum ether. Those who claim that cracking is the chief cause of the formation of the deposits in engines seem willing to accept the statement that oxidation of transformer oils causes sludging. It is also believed that oxidation causes the deterioration of turbine oils.

For a number of years transformer oils have been tested by subjecting them to oxidation or by determining their content of unsaturated hydrocarbons, which may be expected to become oxidized when the oil is in use.

The idea that the deterioration of turbine oils is due to oxidation seems to be a more recent one. Perhaps the next step will be for those who would then be called extremists to say that nearly all lubricants should be subjected to an oxidation test, because all except steam cylinder oils are used in contact with air.

The commonest method for testing transformer oils was devised by Kissling.[5] The oil is kept at 150° C. for 50 hrs. while oxygen is slowly bubbled through it. Sometimes a piece of copper gauze is placed around the delivery tube to act as a catalyst. Modifications of the procedure require heating for as long as 72 hrs. The oxidized oil is first extracted with alcoholic soda, and then the asphaltic matter is precipitated by the addition of petroleum ether. The results are called the "resinification constants," or the "tar-forming" and "coke-forming" numbers.

Nastjukoff's "formolite" reaction[6] is sometimes used to determine the quality of transformer oils. By treatment with formaldehyde and concentrated sulfuric acid, insoluble condensation products are formed from the unsaturated cyclic and alicyclic hydrocarbons. The paraffins, naphthenes, and some other series do not react. The olefins are unsaturated, but do not react, or at least do not yield insoluble products. It does not necessarily follow that they do not take part in the formation of sludge.

EFFECT OF METALS ON OXIDATION OF PETROLEUM OILS

There are many cases in which metals or their compounds are used as catalysts for accelerating oxidation, hydrogenation, and similar operations in organic synthesis. It seemed desirable to learn whether the presence of various metals or their oxides would affect the rate of oxidation of petroleum oils. A few data on this subject, which were presented some years ago, were inconclusive, but they at least indicated that brass accelerates the oxidation. Besides brass, tubes were made of glass, high and low carbon steel, cast iron, vanadium steel, and chrome-vanadium steel. The oil was heated in these tubes.[1] Unfortunately, they had to be made so small that the surface of oil exposed to oxidation was not sufficiently great.

Other results, obtained by heating oil in flasks of the usual size, showed the effect of the presence of fatty oils, sulfur, asphalt, rosin and rosin oil, soap, and ferric oxide.[2] It has also been found that when oil has first been partly oxidized by exposure to air and sunlight,[3] or when the varnish-like coating formed inside of the flask during a previous test is not removed, the amount of asphaltic matter produced by heating is increased. Still more recently it has been found that organic sulfur compounds which do not darken polished copper seem to increase the rate of oxidation.[4]

EXPERIMENTAL METHOD

In the experiments, the results of which are given below, strips of sheet metal 11 by 72 mm., and from 0.2 to 0.6 mm. thick, were placed diagonally inside of the 150-cc. flasks in which the oils were heated. The strips were thus surrounded by a mixture of oil vapors and air. As the vapors tend to be acid, some of the metal was expected to dissolve and be washed down into the oil.

Most of the strips were polished with fine emery paper, washed with water, and wiped dry. Other strips after polishing were coated with oxide by gentle heating over a low flame. Still others were covered with sulfide by leaving them over night in a glass-stoppered bottle into which hydrogen sulfide had been passed for a few moments. Finally, a few tests were made with strips which still had clinging to them the varnish-like coating of oxidized oil from a previous determination.

---

[1] Presented before the Section of Petroleum Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published by permission of the Director of the Bureau of Standards.

[3] Waters: Bureau of Standards, *Scientific Papers* **153** and **160**; *Technologic Papers* **4** and **73**; *Circular* **99**. See also THIS JOURNAL, **2** (1910), 451; **3** (1911), 233, 812; **8** (1916), 587.

[4] See discussion in *Circular* **99**.

[5] *Chem.-Ztg.*, **30** (1906), 932; **31** (1907), 328; **32** (1908), 938; **33** (1909), 521.

[6] Nastjukoff, *Petroleum*, **4** (1909), 1336, 1397; Severin, *Ibid.*, **6** (1911), 197; Heer, *Chem.-Ztg.*, **34** (1910), 893; Marcusson, *Ibid.*, **35** (1911), 729.

[1] Bureau of Standards, *Scientific Paper* **160** (1910), 373; THIS JOURNAL, **3** (1911), 233.

[2] Bureau of Standards, *Technologic Paper* **4** (1911); THIS JOURNAL, **3** (1911), 812.

[3] Bureau of Standards, *Technologic Paper* **73** (1916); THIS JOURNAL, **8** (1916), 587.

[4] Bureau of Standards, *Technologic Paper* **177** (1920), 8; *Circular* **99** (1920), 13.

Copper, nickel, and cobalt oxides were prepared by igniting their nitrates, and ferric oxide from hydroxide which had been thrice precipitated by ammonia. This ferric oxide was in steel-gray lumps which were powdered to pass a 100-mesh screen. For comparison, some determinations were also made with some of Kahlbaum's best grade of ferric oxide which had been in stock for more than 10 yrs.

In all of the experiments with oxides, 25 mg. of the powdered material were added to each 10-g. portion of oil. The weight of the asphaltic matter formed was corrected for this amount of added oxide. This correction was a trifle too large because it was impossible to wash all of the oxide from the flask. However, in only one case did the gain in weight of the flask, on account of the formation of "varnish" and the retention of the oxide, amount to as much as 6 mg., or 0.06 per cent of the weight of oil taken.

The copper oxide left on the bottoms of the flasks a very thin film which was red by reflected light, and blue-green by transmitted light. No attempt was made to ascertain whether this or any of the other oxides was reduced to a lower form or to metal.

All tests were made according to the usual procedure for determining the "carbonization value" of lubricating oils. Ten-gram portions of oil, in 150-cc. Erlenmeyer flasks, are heated in a special air bath which permits free access of air to the surface of the oil. The heating current is regulated so that the bath reaches 250° C. in 30 min. The temperature is automatically maintained at that point for 2 hrs., when the current is turned off, and the bath is allowed to cool for 1 hr. before the flasks are removed.

If the evaporation loss is to be determined, the flasks are then weighed. Ordinarily this is omitted because there has never been, in hundreds of tests, any apparent connection between this loss and the amount of asphalt formed. Thus, in over sixty determinations with each of the two oils used in the present work, the paraffin base oil showed losses varying from 10.4 to 23.8 per cent, and the naphthene base oil 12.8 to 29.1 per cent.

By means of a wash-bottle, the strips were thoroughly rinsed off with 50 cc. of petroleum ether before they were removed from the flasks. The latter were then tightly corked, swirled gently to dissolve the oil, and set aside. Next day the precipitates were filtered off, washed, dried, and weighed.

During the earlier experiments the flasks were weighed to ascertain the amount of varnish-like coating on the inside. This was in no case as much as 10 mg. The metal strips were all weighed. One had 11.9 mg. of varnish on it. The gains were usually only 3 or 4 mg., and often still less.

Two medium motor oils were used: P, a paraffin base oil, and N, a naphthene base oil. They had the following characteristics:

TABLE I—PROPERTIES OF OIL USED

OIL	P	N
Specific gravity	0.897	0.929
Flash point, ° F.	405	340
Fire point, ° F.	475	415
Viscosity, Saybolt Universal		
At 100° F.	303 sec.	341 sec
At 130° F.	155 sec.	150 sec.
At 212° F.	52 sec.	49 sec.
Pour test, ° F.	30	Below zero
Sulfur, per cent	0.18	0.19
Carbon residue, Conradson, per cent	0.32	0.08
Carbonization value, Waters, per cent	0.53	0.25

Table II gives the carbonization values for these two oils when heated in contact with the various metals and metal oxides. Each value is the average of two or more determinations.

TABLE II—EFFECT OF CATALYSTS ON THE OXIDATION OF TWO OILS

EXPT	CATALYST	Carbonization Value Per cent Paraffin Base	Carbonization Value Per cent Naphthene Base
1	None	0.53	0.25
2	Zinc	0.51	0.26
3	Aluminium	0.56	0.24
4	Steel, cold rolled, polished	0.58	0.29
5	Steel, oxidized to blue by heating	0.60	0.29
6	Cast iron, polished	0.60	0.31
7	Cast iron, oxidized to blue by heating	0.54	0.30
8	Nickel	0.60	0.30
9	Cobalt	0.59	0.30
10	Phosphor bronze	0.77	0.41
11	Brass, polished	0.72	0.29
12	Brass, oxidized by heating	0.63	0.27
13	Brass, tarnished with hydrogen sulfide	0.68	0.30
14	Brass, partly coated with "varnish"	0.55	0.24
15	Copper, polished	0.83	0.50
16	Copper, oxidized by heating	0.81	0.51
17	Copper, tarnished with hydrogen sulfide	0.84	0.55
18	Copper oxide	0.91	0.45
19	Nickel oxide	0.88	0.30
20	Cobalt oxide	0.78	0.32
21	Ferric oxide from hydroxide	0.65	0.30
22	Ferric oxide from Kahlbaum	0.74	0.37
23	Oil oxidized in sunlight for 20 hrs.	0.92	0.57
24	"Varnish" on walls of flask	0.61	...

In considering the figures given in the table, it should be borne in mind that differences of 0.02 or 0.03 per cent are negligible.

It is evident that zinc and aluminium are not oxygen carriers, when heated with these two oils.

Cold rolled steel and cast iron, whether polished or heated to the bright blue which follows the deep purple, caused much less increase in the percentage of asphalt than was expected. The very hard, compact ferric oxide which was made by igniting the hydroxide produced a greater effect, which was exceeded by that of the German product.

Metallic nickel and cobalt behaved about the same as iron and steel. Their oxides caused a slight increase in the rate of oxidation of the naphthene base oil and a great increase with the paraffin base oil. These two metals and their oxides were used because cobalt compounds are very efficacious driers of linseed oil, while nickel compounds are not nearly as active. It was surprising to find that nickel oxide was a better oxygen carrier than cobalt oxide. The ends of the nickel strips were blackened where they dipped into the oils. This was true of no other metal.

The results with copper show that the use of this metal in sludging tests is justified, not only because the wires in a transformer are made of it, but because it causes a greater amount of oxidation than any of the other metals. Only copper oxide and preliminary oxidation of the oil in sunlight produced greater effects. It is not easy to understand why copper oxide should cause more oxidation of the paraffin base oil than does a strip of oxidized copper, while the reverse is true of the naphthene base oil.

Phosphor bronze and brass were expected to give results as high as those with copper and copper oxide, but they did not. The most surprising fact was the apparent protective action of the varnish-like coating from a previous test. The varnish alone acted as a catalyst (Expt. 24), but when on the brass strip it seemed to be inert.

Expt. 23 shows how great an effect is caused by first oxidizing the oil by exposure to air and sunlight. It is interesting to note that, owing to absorption of oxygen, the paraffin base oil gained in weight 0.63 per cent and the naphthene base oil 0.28 per cent. These figures should not be compared with those found when the oils were heated with oxidized brass (Expt. 12) and with ferric oxide (Expt. 21). The similarity is only an accidental one.

It is hardly necessary to point out the bearing of the data given above upon the use of oils where they are in contact with heated metals and air. One might say that transformers should be constructed of zinc and aluminium, and that bearing metals should contain no copper.

SUMMARY

The relation between the oxidation of petroleum oils and the formation of deposits in internal combustion engines to the sludging of transformer oils and to the deterioration of turbine oils is briefly discussed.

The acceleration of the rate of oxidation by the presence of catalysts is then taken up.

Finally, data which show the effect of several metals and metal oxides upon the carbonization values of two typical oils are given in tabular form and discussed. Zinc and aluminium caused no increase in the quantity of precipitate. Steel, cast iron, nickel, and cobalt caused a slight acceleration, and phosphor bronze, brass, and copper a considerable acceleration of the rate of oxidation. All of the oxides showed marked effects. The highest values of all were obtained with oil which had been exposed to sunlight and air for 20 hrs. before heating.

The Action of Anhydrous Stannic Chloride on Petroleum and Its Distillates[1]

By **Gregory Torossian**

IDEAL PASTE & CHEMICAL WORKS, 1497 COUTANT AVE., CLEVELAND, OHIO

When crude petroleum or crude petroleum distillates are shaken with concentrated sulfuric acid, the acid gradually attacks the resinous, tarry, and oxygenated bituminous bodies found in petroleum, partly decomposing them, partly absorbing them in a complex mixture which, on standing, separates as a dark lower layer below the unaffected hydrocarbons. By this process practically all of the main impurities of petroleum distillates are removed, and by subsequent washings with alkali solutions, filtration, etc., the final refining is completed. Although special methods of refining are employed for special petroleums, especially those containing a large amount of sulfur compounds, sulfuric acid is the primary reagent which eliminates most of the tarry, resinous, oxygenated bituminous bodies.

When anhydrous stannic chloride, $SnCl_4$, is poured into a crude sample of petroleum or any of its distillates, a precipitate is instantly formed. Its color, quantity, and physical and chemical properties depend upon the character of the petroleum and the particular fraction at hand. Red, orange, yellow, gray, brown, dark brown, and black precipitates are produced from various distillates. These precipitates are formed whether the samples contain moisture or not, the water combining with $SnCl_4$ to form the hydrated chloride, which is incorporated with the precipitate.

Table I shows some of the results thus far obtained.[2]

REMOVAL OF COLOR

The distillates treated with tin tetrachloride are easily filtered through ordinary filter paper on cloth in a suitable filter press, while small amounts can easily be filtered through a wad of cotton. Several gallons of "Machine Oil" distillate treated with the tetrachloride and passed through a small experimental filter press packed with paper and cloth filtering mediums came out as a clear yellow oil.

In all cases, and especially with petroleum distillates containing sulfur compounds, distinct improvement in the color and odor of the oils was observed. A kerosene distillate obtained from a sample of Baku petroleum showing a color test of 50 mm. (chromometer similar to Stammer's) gave a color test of 138 mm. when treated with about 0.35 per cent $SnCl_4$ and filtered through paper. After washing with a dilute alkali solution, the color rose to 178 mm., which is the nearest to Mark 2, or what is known in the oil market as "superfine white."[1] The so-called sulfuric acid test showed the absence of tarry, resinous, and oxygenated bituminous bodies, and it passed the "soda" test, the odor being that of the best refined kerosene. A sample of "Machine Oil" distillate was treated with about 1.5 per cent of tin tetrachloride, the resulting precipitate freed from the oil, and the latter washed with caustic soda solution. It now gave a color test of 21 mm., the color being crystalline, bright, and light brown (Russian specifications, somewhat different from American).

No.	Product	Source	Average Sp. Gr.	Boiling Range °C.	Approximate Amount Per cent $SnCl_4$	Precipitate[1]	
1	Gasoline distillate	Petroleum in general	0.750	Up to 150	0.10–0.15	Reddish	Small amounts to none, if carefully distilled; compact film formed on vessel
2	Kerosene distillate	Any petroleum not containing much S	0.820	150–300	0.3–0.5	Blood-red when settled	Sticky; compact transparent film formed on vessel; acid to litmus paper
3	Kerosene distillate	Sulfur-containing petroleums		......	0.3–0.5 or more	Light yellow to bright orange; also red	Red ppt.: sticky; film forming; yellow and orange ppts.: loose particles, containing sulfur compounds
4	Fraction from 300° C. up to Machine Oil: "Solar Oil," "Vaseline Oil," etc.	Russian petroleum	0.885 0.890	......	1.0–1.5	Gray to dark brown	Gray ppt.: loose particles, easily stirred; brown ppt.: partly plastic, partly porous
5	Same as No. 4	Ohio and Canada petroleums	0.885	......	1.0–1.5	Yellow to orange; brown	Appears to contain most of sulfur compounds; dark ppt.: plastic as usual; yellow and orange ppts. are of particles loosely held together, easily stirred
6	Machine Oil Cylinder Oil Distillates	Petroleum in general	0.895–0.911	......	1.5–2 or more	Dark brown to black	Plastic, tenacious, forms soft wax when worked up in the hand; melts and solidifies into a lustrous product; becomes brittle and porous on continued heating

[1] All these ppts. are decomposed when treated with concentrated sulfuric acid, anhydrous stannic chloride being set free.

The action of tin tetrachloride upon various crude distillates of petroleum is so characteristic that it is not difficult to tell offhand, from the color, bulk, and physical properties of the precipitate, which of a given series of crude distillates a certain fraction is, and from what kind of petroleum the distillates are derived.

---

[1] Received April 11, 1921.

[2] These data are not complete, as work has not yet been finished.

[1] According to Redwood, II, 214, "superfine white" corresponds to 190 mm. on Stammer's chromometer. There is no explicitness on this point of specifying the color of kerosene.

An excess of tetrachloride has no action upon the hydrocarbons of the petroleum, once the impurities have been eliminated. The end of the reaction is easily seen by the characteristic fuming of the tin tetrachloride when the latter has been added in excess. That the chloride has no action on the saturated hydrocarbons is evident chiefly from the fact that it gives no precipitate with the purified petroleum products. White paraffin wax and white vaseline remain absolutely unaffected when treated with the chloride, while the yellow vaseline gives a slight reaction, indicating incomplete refining or oxygenation of the original pure product. A few drops of tin tetrachloride added to a sample of petroleum product will show instantly whether the sample is a crude product or refined, and, if refined, how far the refining has been carried.

NATURE OF ACTION OF TETRACHLORIDE

The action of tin tetrachloride upon the impurities of petroleum is chiefly chemical, although some physical phenomena seem also to be involved in the process of precipitation. It forms compounds with various impurities of the petroleum without itself undergoing decomposition. This is shown by the fact that when concentrated sulfuric acid is added to the precipitates, the anhydrous tetrachloride is liberated, as shown by the characteristic fuming, and by testing the regenerated liquid with a sample of crude distillate. When burned, the compounds leave an ash containing stannic oxide, although on careful burning the tin appears in the metallic state as a gray spongy mass.

The tetrachloride also polymerizes the oxygenated bituminous bodies of petroleum. This is seen from the fact that a very small quantity of $SnCl_4$ is necessary in order to produce a bulky precipitate from a heavy crude distillate and also from the action of the chloride directly upon tars, which are converted into solid asphaltum or pitch-like products. Pine tar, for instance, is converted into a solid, lustrous, pitch-like body on treatment with 10 or 15 per cent of $SnCl_4$. The reaction is very vigorous and is accompanied with liberation of much heat.

Felix C. Thiele[1] mentions the action of tin tetrachloride briefly in connection with the terpinenes, $C_{10}H_{16}$, and polyterpinenes, $(C_{10}H_{16})_x$, found in petroleum. While it is true that certain hydrocarbons classed as terpinenes do combine with tin tetrachloride, the action of this reagent on crude petroleum products cannot be explained on the assumption that it is solely chemical in nature. To be sure, chemical compounds are formed when petroleum impurities come in contact with $SnCl_4$, and polymerization also takes place, but it seems that some physical factors must enter into the process of precipitation of bulky, tenacious, or plastic bituminous bodies from the crude petroleum or its heavier distillates. The fact that such small quantities of tetrachloride are required to bring down bulky precipitates from the heavier distillates, combined with the fact that although in adding the reagent to a heavy sample all particles of reagent and oil are not brought into close contact at once, the precipitation is almost instantaneous, indicates that the process is physical as well as chemical. It appears that, once the tetrachloride has brought down part of the impurities, the rest will follow as a result of disturbed equilibrium.

The tetrachloride seems to react primarily with the oxygenated bituminous bodies, sulfur compounds, unsaturated organic acids, and terpinenes, found in petroleum. Terpinenes, especially, enter into a violent reaction, forming yellow or brown precipitates. Thus, spirit of turpentine reacts with stannic chloride with almost explosive violence, with the liberation of much heat, and the formation of a brown precipitate, consisting of loose particles which can be separated by filtration from the unaffected portion. Incidentally, this reaction shows that turpentine contains hydrocarbons, some of which are reactive and some not reactive with stannic chloride. The unsaturated organic acids, such as are found in drying oils, are also attacked with great violence. Linseed oil, for example, is bodily converted into a brown, viscous product when treated with tin tetrachloride. The tetrachloride, however, does not eliminate all the so-called naphthenic acids found in petroleum. Thus, a sample of kerosene distillate which had been treated with $SnCl_4$, filtered, and washed with distilled water, showed 0.10 per cent acidity in terms of SO_3, while a sample of lubricating distillate, also treated with the chloride, filtered, washed, etc., gave an acidity of 0.20 per cent. It is interesting to note here that while tin tetrachloride destroys practically all the unpleasant odors from the crude petroleum products, it does not eliminate the last traces of "raw" odor, and only after washing with an alkali solution does the odor become "sweet." This is explained by the fact that $SnCl_4$ does not completely remove the naphthenic acids, to which the odor is due.

SUMMARY

1—Tin tetrachloride precipitates the tarry, resinous, oxygenated bituminous bodies, and also sulfur-containing compounds from crude petroleum and its crude distillates, by forming compounds with them, and also by polymerizing action upon them.

2—Tin tetrachloride has no effect on the saturated hydrocarbons of petroleum. It combines violently with unsaturated organic acids and hydrocarbons of the terpinene series with liberation of heat, and also polymerizes the tars.

3—The tin tetrachloride reaction affords a means for qualitative and quantitative tests for petroleum products.

4—Tin tetrachloride performs all the functions of sulfuric acid in the process of refining oils, and in addition it eliminates the sulfur compounds, thus serving as a reagent for the purification of all kinds of petroleum products.

---

[1] Am. Chem. J., 22 (1899), 489.

The Société de Chimie Industrielle

The Annual Meeting of the French Société de Chimie Industrielle to be held at the Conservatoire National des Arts et Métiers, October 9 to 12, 1921, will bring together its home and foreign members.

The meeting will constitute a true congress of industrial chemistry, embracing thirty-four technical sections, as follows: analytical chemistry; factory equipment; laboratory equipment; gas and coke-oven industries; hydrocarbons and petroleum; distillation of wood and its derivatives; refrigerating industries; water; metallurgy and electrometallurgy; precious metals; electrochemistry; lime, cement and building materials: glass, ceramics, and enamels; rare earths and radioactive substances; dyes; pharmaceuticals; photographic products; powders and explosives; essences, natural and synthetic perfumes; resins, pigments, lacs, varnishes, and waxes; rubber and rubber substitutes; fats, soaps, candles, and glycerol; cellulose and paper; plastic materials, and artificial textiles; bleaching, dyeing, printing and sizing; dyeing and tanning extracts; tannery industries; fermentation, wine, cider, brewery and distillery industries; sugar; starch and glucose industries; dairy industries; food materials; agricultural chemistry, soils, fertilizers.

In connection with this meeting, the society has arranged a chemical exposition, under the patronage of the Minister of Commerce. This Exposition, which is to be held at the Conservatoire National des Arts et Métiers, October 7 to 16, 1921, will consist of two sections: laboratory equipment and factory control, and dyes. Already a majority of French manufacturers have enrolled as exhibitors. The novelty and diversity of apparatus and products which are to be exhibited cannot fail to attract a large number of visitors interested in the development of the different branches of chemistry.

Production of Coumarins from Maleic and Malic Acids[1]

By G. C. Bailey and F. Boettner

Research Department, The Barrett Co., 40 Rector St., New York, N. Y.

The following work was undertaken in order to find out it it were possible to develop a commercial synthesis of coumarin from malic acid,[2] and, if such a synthesis proved uneconomical, to determine whether other coumarin derivatives were of value as perfumes or flavors. As a matter of general interest a few condensations were attempted with maleic acid.

The malic acid was the synthetic inactive acid made by the hydration of maleic acid obtained by the catalytic oxidation of benzene.[3] The *m*-cresol was of coal-tar origin and was partly separated from the para isomer by the method of F. Elger.[4]

Procedure

The aliphatic acid was added to the phenol and condensing agent contained in a test tube inserted in an oil bath at the desired temperature. Foaming usually resulted upon stirring, and the solutions became yellow or orange colored. After the evolution of gas had ceased, the contents of the tube were poured over ice and the resulting precipitate filtered off. The precipitate, in the runs where phenol was used, was usually found to be fumaric acid. The filtrate was shaken up with ether and the ether solution examined for coumarin. The absence of the characteristic coumarin odor was considered to be an indication of failure to secure that product.

Experimental

SERIES I—Equal weights of phenol and maleic acid were heated at temperatures ranging from 100° to 160°, for times ranging from 40 min. to 5 hrs., with 96 per cent sulfuric acid and with zinc chloride without securing any coumarin.

SERIES II—A number of runs were made with phenol and malic acid in a manner similar to the above without the isolation of any coumarin. Beside the condensation agents of Series I, the following were also tried: 100 per cent sulfuric acid, sodium acetate and zinc chloride, potassium acid sulfate, stannic chloride, pyridine in 100 per cent sulfuric acid, phosphorus pentoxide, and aluminium chloride. The manner of adding the ingredients was varied without securing the desired coumarin.

SERIES III—The authors followed the procedure of Fries and Klostermann[5] which was in general the same as that used in the preceding series, except that the precipitate which formed when the reaction mixture was poured on ice was taken up in 50 per cent alcohol and crystallized. This gave a fairly pure 4-methylcoumarin, which became very pure upon one recrystallization from 50 per cent alcohol containing a little boneblack. The yields given in Table I are based upon the recrystallized 4-methylcoumarin of melting point 128° C. The unchanged cresol was regained by steam distillation of the original filtrate. The malic acid which did not react with the cresol was entirely lost by this process, and no attempt was made to recover any products from it.

Experiments showed that with a *m*-cresol of purity of 84 per cent and a dry malic acid, a yield of approximately 40 per cent of crystallized methylcoumarin could be obtained. The best conditions found were those in which the cresol and sulfuric acid were mixed and the malic acid fed in slowly with the bath held at 135° C. With a pure *m*-cresol the yield was about 54 per cent. If all the malic acid was added in one portion the yield was very greatly diminished.

Value of Methylcoumarin as a Perfume and Flavoring Extract

TOXICITY—As coumarin is a constituent of flavors used in foods, it was desirable to know the relative toxicities of coumarin and the methylcoumarin. The coumarin chosen for test was a product from natural sources. The toxicity[1] tests were carried out as follows, using the white mouse: The dose, which was injected subcutaneously at the base of the tail, was calculated per gram of body weight. The mice were observed for a period of 1 wk. after inoculation.

Coumarin and methylcoumarin are both insoluble in water. Fifty per cent alcohol will dissolve the substances, but this is extremely toxic to white mice. An inert substance such as acacia had, therefore, to be chosen to emulsify the powders. The powders were ground to pass through a 40-mesh sieve and suspended in a 10 per cent solution of acacia in such dilutions that the injections would contain the doses indicated in the table. A control inoculation was given of the 10 per cent acacia. The suspensions were so gaged that the total amount injected was from 0.04 to 0.05 cc. per g. of body weight.

Material Tested	Weight of Mouse Grams	Dose per G. Body Weight Grams	Result	Time Hr.	Time Min.
Methylcoumarin	29	0.0010	Survived		
	20.5	0.0020			
	21.5	0.0030			
	22	0.0040			
	21	0.0050	Lethal	Over night	
Coumarin	22	0.0002	Survived		
	12.5	0.0004	Lethal	2	
	13	0.0006		2	45
	14	0.0008		2	
	24	0.0010		2	15
	22	0.0020		2	55
10% Acacia (control)	22		Survived		

The results as a whole turned out very satisfactorily indeed. It is safe to state that methylcoumarin is not more than one-tenth as toxic as coumarin when injected subcutaneously into white mice. The minimum lethal dose for white mice is between 4 and 5 mg. per g. of body weight for methylcoumarin, and, for the coumarin, between 0.2 and 0.4 mg. per g. of body weight.

PERFUME VALUE—The perfume value was tested by expert perfumers and said to be, in dilute solutions, of almost the same odor as the natural coumarin. The taste was similar but slightly less intense than the natural coumarin. The odor of the dry crystals was considerably less intense than the natural or synthetic coumarin.

Conclusions

1—No coumarin derivative was obtained from the action of phenol and maleic acid in the presence of dehydrating agents.

2—Coumarin in no appreciable quantities was produced by the action of various dehydrating agents upon phenol and malic acid.

3—A study of the best conditions for the reaction of *m*-

---

[1] Received May 13, 1921.

[2] Von Pechmann, *Ber.*, **17** (1884), 929; Von Pechmann and Welsh, *Ibid.*, 1646–52; Von Pechmann and Cohen, *Ibid.*, 2187–91; Clayton, *J. Chem. Soc.*, **93** (1908), 2016; Dey, *Ibid.*, **107** (1915), 1606; Simonis, *Ber.*, **48** (1915), 1583–85; Fries and Klosterman, *Ibid.*, **39** (1906), 871–5.

[3] Weiss and Downs, U. S. Patent 1,318,633.

[4] F. Elger, assignor to Hoffman-LaRoche & Co., U. S. Patent 1,025,615.

[5] *Loc. cit.*

[1] These tests were made by the Lederle Laboratories (now the Pease Laboratories) of 39 West 38th St., New York City.

TABLE I—ACTION OF META-CRESOL AND MALIC ACID

Expt.	Malic Acid Charged Grams	m-Cresol 84.24% Charged Grams	H_2SO_4 96% Charged Grams	Time of Heating Min.	Temp. Bath ° C.	Methyl-coumarin Grams	Yield on Malic Charged Per cent	REMARKS
1	2	3.5[1]	5.5	30	140	...	Trace	Malic acid added in one portion
2	5	7	21	240	140	1.27	21.2	Malic acid fed in small portions
3	15	14.3	30	30	139	3.6	20.4	H_2SO_4 added to the cresol and malic acid
4	25	25	50	125	135	...	None	Similar procedure to No. 3
5	5	5	7.5	115	140	1.16	19.5	Cresol sulfonated at 25° and malic acid fed in slowly over period of 2 hrs.
6	5	15	15	255	140	2.02	33.9	Cresol sulfonated at 140° for 20 min. and malic acid fed in slowly for 4 hrs.
7	5	5	15	255	140	2.33	39	Duplicate of No. 6. In remainder of experiments malic acid was fed into the charge slowly
8	5	5	15	180	136	2.354	39.4	Run made in wrought iron
9	25	25[2]	75	180	135–40	16.11	53.9	

[1] 46 per cent m-cresol charged.

[2] 98 per cent m-cresol used, solidifying point 9.8° C.

cresol and malic acid in the presence of sulfuric acid for the production of methylcoumarin showed that a yield of 50 per cent, reckoned on the malic acid, could be obtained with a very pure m-cresol, and about 38 to 40 per cent with an 84 per cent m-cresol.

4—Both the toxicity and perfume values of the methylcoumarin indicated that it could replace coumarin for flavors and perfumes.

Condensation Temperatures of Gasoline- and Kerosene-Air Mixtures[1,2]

By Robert E. Wilson and D. P. Barnard, 4th

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

OBJECT OF WORK

A knowledge of the temperature at which various mixtures of internal combustion engine fuels and air are completely vaporized, or just begin to condense, is of great importance in connection with the design of carburetors and intake manifolds and the automotive fuel problem in general. To secure satisfactory distribution between the different cylinders a fuel must be completely vaporized. This may be accomplished by heating the fuel, the air, or the resulting mixture. If, however, the amount of heating is more than that required to vaporize the fuel, serious losses are encountered from the decreased capacity of the engine for the hot mixture, and the increased tendency toward knocking. From this standpoint it is important to know what minimum temperature must be reached in order to make possible complete vaporization, and then improve the efficiency of the mechanical devices for vaporization of the fuel until substantially complete vaporization is obtained without appreciably exceeding this theoretically minimum temperature.

The suitability of kerosene and other fractions as fuels for internal combustion engines, the proper end-point for gasoline, and other important fuel problems, also depend to a considerable extent upon the *dew point* of the fuel-air mixtures (the temperature at which vaporization is complete or at which condensation begins on cooling).

In spite of the obvious importance of this information, the writers have been unable to find any published information as to the dew point of mixtures of the commoner fuels with air in the customary proportions. In fact, practically the only discussion of the problem is a very interesting recent article by Howard.[3] This paper points out the importance of the problem and describes some experiments on gasoline which lead the author to draw certain practical conclusions. Although these conclusions are sound, the experimental results do not give any definite information as to the condensation point of gasoline under service conditions. There appear to be no data whatever on kerosene-air mixtures.

METHODS OF DETERMINING THE CONDENSATION POINTS OF FUEL-AIR MIXTURES

The most direct method of determining the dew point of mixtures of air and, say, gasoline would be to introduce a small, accurately weighed amount of gasoline into a flask containing a known volume of air, close all outlets, raise the temperature of the mixture until the gasoline was completely vaporized, and then cool very slowly until a mist of gasoline began to deposit on the walls of the flask; or, better, on an internally cooled mirror, such as that used by McBain[1] in his work on soap solutions. By recording the pressure and temperature at which condensation began it should be possible to obtain a fairly accurate value for the dew point of a particular mixture at a given pressure. The most serious objection to this method lies in the fact that a new sample must be accurately weighed out for each separate determination and that a large number of determinations must be made in order to determine the properties of a given fuel over the ordinary range of mixture ratios and pressures which are of interest. The Bureau of Standards has made some determinations by this method, but reports that the results thus far obtained are not considered satisfactory.[2]

It might be suggested that the desired information could be obtained more simply by making vapor pressure measurements, as in the case of pure compounds. The difficulty of this suggestion lies, however, in the fact that gasoline is a mixture of compounds which differ widely in volatility, and the vapor pressure of the original gasoline bears no relation to the vapor pressure of the fraction which first condenses out on cooling a completely vaporized mixture. If, however, it were possible to secure any considerable quantity of this fraction which first condenses out from (and hence is in equilibrium with) the completely vaporized mixture, measurements of its vapor pressure would obviously give the data desired.

It might at first sight be assumed that the composition of the fraction which first condenses out would be the same as that which was last distilled off in an ordinary distillation; but this is far from being the case, as a little consideration

---

[1] Presented before the Section of Petroleum Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Contribution No. 36 from Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] "The Volatility of Internal Combustion Engine Gasoline," *J. Soc. Automotive Eng.*, **8** (February 1921), 145.

[1] *J. Am. Chem. Soc.*, **42** (1920), 426.

[2] Private communication from Dr. H. C. Dickinson.

will show. The material which last distils out of the flask is in equilibrium with the vapor which is leaving the flask *at that moment*, and not with the completely vaporized gasoline as a whole. For this reason, the data obtained by Howard on the vapor pressure of the least volatile portion of the gasoline (the last 10 per cent distilled off) do not in any sense determine the temperature at which the mixture as a whole would begin to condense.

If a large volume of completely vaporized gasoline were run through a condenser whose temperature was gradually lowered until condensation just began, it is conceivable that a small amount of condensate might be secured which would represent fairly well the composition of the equilibrium mixture whose vapor pressure is desired. Any such device would, however, be open to serious question because of the necessary existence of a temperature gradient from the center of the stream to the walls, and the probability is that most of the condensate would come from that part of the vapors nearest the walls, rather than representing true equilibrium with the mixture as a whole. On account of these difficulties, this Laboratory has developed a new method of obtaining a considerable amount of the desired equilibrium solution, and by measuring its vapor pressure is able to calculate accurately the initial condensation temperature for any given mixture and total pressure within the range of ordinary practice. By combining these data with data on the vapor pressure of the original gasoline it is also possible to determine *approximately* the fraction condensed under any given set of conditions.

The methods used are described in the following section.

It must be emphasized at the outset that results secured by such methods represent the conditions prevailing at *equilibrium* and it is quite possible to obtain "wet" mixtures at temperatures well above the dew point, because the drops of the fuel which are sprayed into the air stream do not have sufficient time to absorb heat and vaporize before the mixture reaches the engine. The results simply indicate what is theoretically obtainable if the time, the degree of atomization, etc., are sufficient to permit equilibrium to be approached fairly closely.

Practical experience with present-day fuels indicates that on account of the limited time available it is necessary to separate out and apply heat to the unvaporized drops by direct contact with metal surfaces, as in various types of hot spot manifolds, etc.

The experimental methods and the results on kerosene were worked out in this Laboratory in the course of an investigation financed by The Yale and Towne Manufacturing Company, and are published with their kind permission. In view of the importance of the results the Laboratory at its own expense extended the investigation to include two samples of gasoline.

EXPERIMENTAL METHODS

FUELS INVESTIGATED—In this work three different and representative fuels were selected for investigation; their distillation curves are shown in Fig. 1.

Socony Motor Gasoline, obtained from the Boston branch of the Standard Oil Company of New York, and having an initial boiling point of 60° C., an end-point of 211° C., and specific gravity of 0.743 (60° Bé.). Its average boiling point is fairly typical, but its boiling range is somewhat narrower than the average present-day product.

Socony Kerosene, also obtained from the Standard Oil Company of New York. The initial boiling point was 168° C., the end-point 282° C., and the specific gravity 0.800 (45° Bé.).

High End-point Gasoline—This was an artificially prepared high end-point gasoline consisting of a blend of 100 parts of Socony Motor Gasoline and 25 parts of the lighter 50 per cent fraction obtained by distilling Socony kerosene at atmospheric pressure. The initial boiling point of this mixture was 62° C., the end-point 252° C., and the specific gravity 0.752 (57° Bé.).

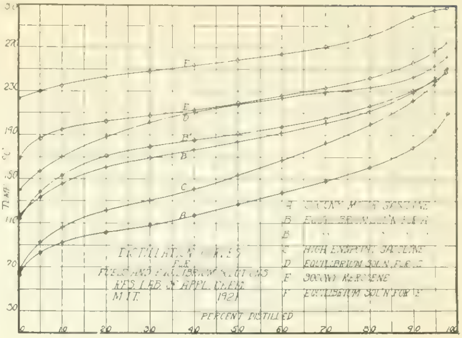


Fig 1

AVERAGE MOLECULAR WEIGHTS—In order to calculate the partial pressure of the fuel in, say, a 15 : 1 (by weight) mixture, it is necessary to know the approximate *average* molecular weight of the fuel. The average molecular weights as used in this work were determined with sufficient accuracy[1] by first obtaining their distillation curves (Fig. 1) and from these curves plotting the differential distillation curves (Fig. 2).[2] The average boiling point was taken as the point at which a perpendicular passed through the center of gravity of the area bounded by the curve and the X-axis cut this axis. The distillation tests were made in a standard Engler still, using 100-cc. samples. The average boiling points as determined above, and the molecular formulas and weights of saturated paraffin hydrocarbons most nearly (within 2° or 3° C.) corresponding to these weights are given below:

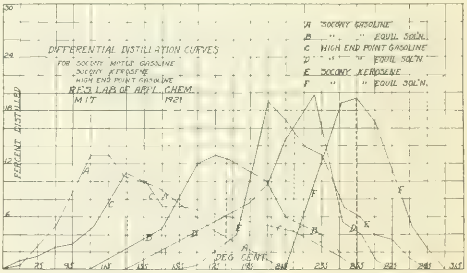


Fig 2

Fuel	Average Boiling Point, ° C.	Corresponding Formula	Average Molecular Weight
Socony Kerosene	220	$C_{12}H_{26}$	170
Socony Gasoline	128	C_8H_{18}	114
High End-point Gasoline	147	C_9H_{20}	128

---

[1] Rigidly this method is undoubtedly inaccurate, but since an error of 10 per cent in the molecular weights would only change the condensation temperatures by 2° or 3°, it was not considered worth while to spend the amount of time involved in an accurate determination, especially in view of the great variations between different samples of commercial gasolines.

[2] This form of the distillation curve, obtained from the customary form by plotting the per cent coming over between each 10° C. (or 20° F.) against the median boiling point of the fraction (*i. e.*, plotting the per cent over between 80° and 90° C. against the temperature of 85° C.) is much more useful in comparing different fuels and detecting the presence of added constituents, such as benzene (which give a sharp peak in the curve near their boiling points).

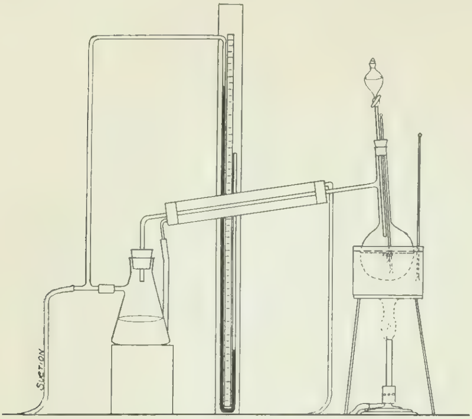


FIG. 3—APPARATUS FOR PREPARATION OF EQUILIBRIUM SOLUTIONS

The partial pressures of the fuels in the different mixtures were calculated after the following example for a 15 : 1 kerosene-air mixture:

Partial pressure of kerosene at 1 atm. total pressure

$$= \frac{\frac{1}{170}}{\frac{1}{170} + \frac{15}{29}} \times 760 = 8.55 \text{ mm.}$$

THE EQUILIBRIUM SOLUTION—As pointed out in the previous section, in order to determine the initial condensation point of a fuel-air mixture, it is necessary to prepare a considerable amount of a so-called "equilibrium solution" whose composition is in precise equilibrium with the uncondensed fuel at its dew point. This solution was prepared in a glass still arranged for continuous operation (Fig. 3). The amount of liquid in the flask was kept constant at all times by carefully adjusting the rate of supply to that of condensate discharge, the level being measured by means of a small glass hook gage. The temperature of the oil bath was also kept fairly uniform.

At first the composition of the fuel in the flask, and hence its boiling point, was identical with that of the original fuel; the vapor which passed off was, however, richer in the more volatile constituents, and hence as the distillation proceeded the solution contained more and more of the less volatile materials, and its boiling point rose. After four or five times as much liquid had passed through the flask as was held there, the temperature of the boiling liquid soon reached a constant maximum point, after which the distillation was continued, keeping all conditions constant, until two or three more times the volume of the liquid in the flask had been distilled over.

By this time a dynamic equilibrium had certainly been definitely established, and since input must equal output, the composition of the vapor leaving the flask must then have been exactly equal to that of the original liquid entering. But the liquid in the flask was in equilibrium with this outgoing vapor, and it therefore had the same composition as that of the liquid which would first condense out from the vapor at its dew point. Furthermore, enough of the liquid was then secured not only to measure its vapor pressure, but also to determine its distillation range compared with that of the original fuel.

The only remaining uncertainty involved is whether or not the composition of this equilibrium mixture is substantially the same at different temperatures. To settle this point two equilibrium solutions were prepared from the same gasoline—one with the flask at atmospheric pressure, and one at about 13 cm. absolute pressure (this changing the boiling points by about 60° C.). The distillation curves for these two solutions are given respectively by B′ and B in Fig. 1. Careful measurement of the vapor pressures showed that the variations between the dew points as determined from the two solutions in no case exceeded 3° C. All other equilibrium solutions were prepared at about 13 cm. pressure, so as to approach reasonably closely to the comparatively low temperatures at which condensation takes place from air-fuel mixtures.

It will be noted from the differentiated form of the distillation curves (Fig. 2) that the average boiling point of the equilibrium solution falls approximately at the 85 per cent point of the original fuel, and contains a considerable amount of material boiling as low as the 50 per cent point. This would be expected, since the first per cent or two distilling off of the equilibrium solution should have the same composition and average boiling point as that of the original solution. The presence of some of the more volatile constituents is, of course, due to the fact that they dissolve in, and have their vapor pressure lowered by, the less volatile constituents. The foregoing illustrates the fallacy of assuming that the extreme high end of the distillation curve determined the initial condensation temperature of the fuel, or that any arbitrary selection of a high fraction of fuel can properly represent the composition of the equilibrium solution.

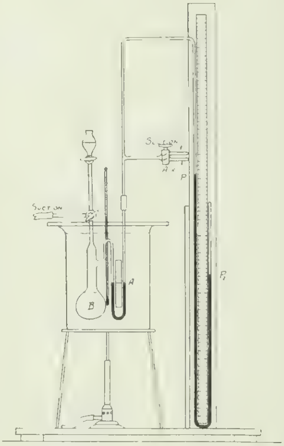


FIG. 4

DETERMINATION OF VAPOR PRESSURE CURVES—Two vapor pressure curves for each fuel were experimentally determined: the vapor pressure curve of the original fuel (which corresponds to the vapor pressure exerted by the completely condensed fuel); and the vapor pressure curve for the equilibrium solution which represents the first drop which condenses out of a completely vaporized mixture.

The vapor pressures were measured at different temperatures in the apparatus sketched in Fig. 4. The bulb was about 80 per cent filled with the liquid to be measured, and the U-tube was half filled with mercury. This U-tube, being immersed in the constant temperature bath, served to prevent the vapor from condensing in the manometer, as it would otherwise do. The pressure in the space between the U-tube and the manometer was adjusted by means of the stopcocks, so as to keep the liquid in the U-tube exactly leveled whenever readings were taken. The pressure exerted by the liquid was then equal to the barometer reading minus the difference between the height of the two manometer columns. Care was taken, when starting a series of observations, to boil off under a high vacuum a very small part of the liquid, so as to free the apparatus of all traces of air. As the bulb held about 40

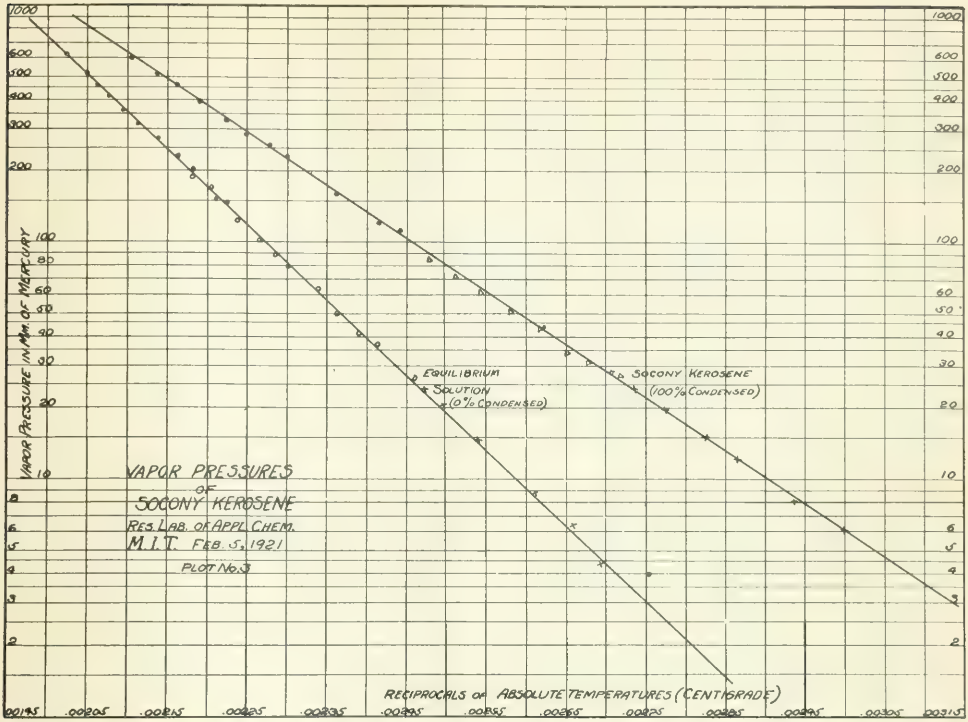


Fig. 5

cc. and the amount lost in this manner was never over 0.2 cc., the error involved was so small as to be entirely negligible.

Most of the measurements were made by increasing the temperature in a stepwise fashion, only a few minutes being required to reach equilibrium at a given temperature. All results were checked by repeating the experiments on separate samples. It was found impracticable to check all points by *lowering* the temperature in a stepwise fashion, as temporary condensation of the vapor in the glass walls of the vessel and in the manometer arm, instead of in the liquid of the flask, made necessary a long wait before equilibrium was obtained. In two attempts which were made to check by this means, the pressure reading kept dropping very slowly for over an hour, but finally reached an equilibrium value which approximated very closely to the value obtained in a much shorter time by raising the temperature.

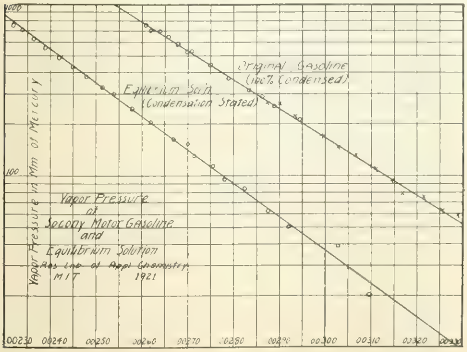


Fig. 6

PLOTTING OF RESULTS—In order to make possible a critical study of the vapor pressure observations and also extrapolations of them with much greater accuracy than is obtainable on an ordinary vapor pressure plot where the curvature is high, the results of observations were plotted on semilogarithmic paper, the vapor pressures being plotted along the log scale, against the reciprocals of the absolute temperatures in degrees Kelvin along the arithmetic scale. Then if the modified form of the Clapeyron equation, which assumes the validity of the Perfect Gas Law,[1] holds for the mixture in question, the experimental points plotted as above should lie along a straight line if the heat of vaporization of the liquid is constant over the temperature range covered, or along a slightly curved line if the heat of vaporization varies with the temperature.

---

[1] *Viz*: $\frac{d \log_e P}{dT} = \frac{Q}{RT}$ or $\frac{d \log_{10} P}{dT} = \frac{Q}{2.3 R (T)}$

in which P = vapor pressure exerted by the liquid, T = absolute temperature in degrees Kelvin (= temperature in ° C. + 273), Q = molal heat of vaporization, and R = gas constant (same units as Q).

The equation is rigidly applicable in this form only to pure compounds, but, in the case in hand, the substances present in the mixture are so very similar in all respects that any deviations would probably be unimportant. The term $\frac{Q}{2.3 R}$ is the slope of the line.

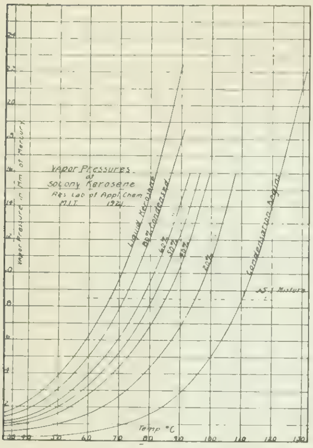


FIG. 7

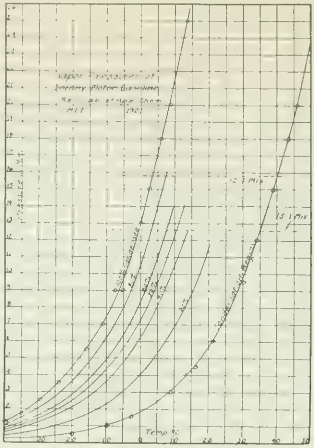


FIG. 8

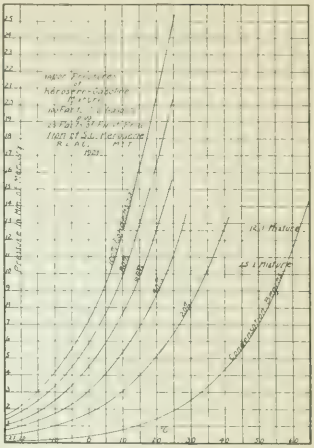


FIG. 9

The fact that these log plots are straight lines[1] indicates that the heat of vaporization is actually substantially constant over the temperature range covered, and this in turn means that the specific heats of the liquid and vapor at any given temperature are nearly equal. The fact that the points all lie on a straight line makes possible the accurate extrapolation of the vapor pressure curve into the low pressure range, where, because of their small magnitude, the pressures are relatively difficult to measure with precision. As the gas laws hold more and more rigidly the lower the pressures, these extrapolated curves are much more accurate than could be determined experimentally without the use of special apparatus.

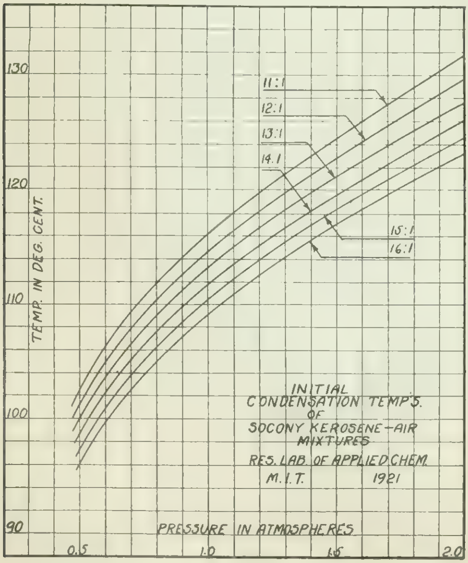


FIG. 10

As is pointed out in the succeeding article, the heats of vaporization as determined from the slopes of these curves agree very closely with those determined by calorimetric methods by different investigators.

INTERPOLATION FOR PARTIAL CONDENSATION POINTS—The upper curves on the log plots (*i. e.*, the vapor pressure curve for the equilibrium solution) represent the vapor pressures of the first drop which condenses out of an air-fuel mixture. The lower curves (for the original fuel) represent the vapor pressures of the 100 per cent condensed liquids. Experimental determinations of the vapor pressures of partially condensed vapors would be extremely difficult. Approximate figures for the various partial condensation temperatures were therefore determined by assuming that the liquid obtained by condensing 40 per cent[1] of the vapor exerted a pressure corresponding to a value 40 per cent of the distance from the totally vaporized line to the completely condensed line. A study of the accurate data available in the literature on the vapor pressure of mixtures of octane and decane[2] showed that this held true to within 5 or 6 per cent. This is certainly near enough to the truth for the purpose at hand, as far as paraffin hydrocarbons are concerned. Figs. 7, 8, and 9 show the vapor pressures exerted by the various fuels, when condensed to different extents, over the range covered by the air-fuel mixtures used in internal combustion engines, plotted directly against the temperatures in degrees centigrade. In order to determine, for example, the temperature at which Socony kerosene is 40 per cent condensed from a 15 : 1 mixture at 1 atmosphere pressure, it is only necessary to find the temperature corresponding to the point on the "40 per cent condensed" curve which indicates a vapor pressure equal to 60 per cent of the vapor pressure of the entirely vaporized fuel—in this case 8.55 mm.

$$0.6 \times 8.55 \text{ mm.} = 5.10 \text{ mm.}$$

5.10 on the "40 per cent" curve corresponds to a temperature of 73° C. Socony kerosene is therefore 40 per cent

---

[1] This is probably only true for fuels which consist essentially of similar hydrocarbons, and not for blends containing benzene, alcohol, etc.

[1] The various figures for "per cent condensed" used hereinafter refer to the percentage lowering of the partial pressure (and hence of the number of molecules) of the vapor in the air, rather than the per cent by weight of liquid recovered. Since the first part of condensate consists on the average of heavier molecules, 50 per cent condensed in the above sense would correspond to possibly 55 per cent by weight condensed.

[2] Landolt-Börnstein, **1912**, 384.

(approximately) condensed from a 15 : 1 mixture under one atmosphere pressure at a temperature of 73° C.

Discussion of Results

The data are all presented in graphic rather than tabular form and are for the most part self-explanatory.

The experimentally determined vapor pressure values are indicated on the log plots, Figs. 5 and 6. It will be noticed that they fall very satisfactorily on straight lines. Although the lines appear to converge before reaching the zero axis, if measurements had been made at pressures above 1.5 atmospheres, it is probable the lines would have begun to curve apart, due to large deviations from the perfect gas laws.

Figs. 7, 8, and 9 are replotted directly from the best representative lines on the log plots, and Figs. 10, 11, and 12 are plotted from values calculated as indicated above from the vapor pressure curves.

These curves, as their titles indicate, show, respectively, the initial condensation temperatures for Socony kerosene and Socony gasoline under different pressures over the range from 0.5 atmosphere to 2 atmospheres, and the temperatures of partial condensation at atmospheric pressure for all three fuels for a 12 : 1 and a 15 : 1 air-fuel mixture (representing fairly closely the composition for maximum power and theoretically perfect combustion, respectively).[1]

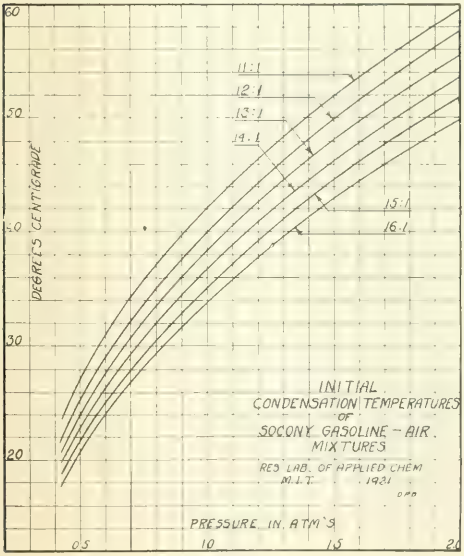


Fig. 11

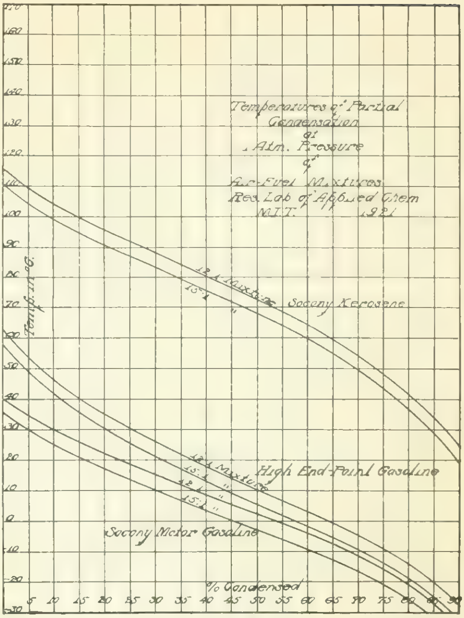


Fig 12

These results indicate clearly that any difficulties in securing complete vaporization of the present commercial gasoline are not due to any inherent limitation in the gasoline itself, or to too low manifold temperatures, once the engine is warmed up. Indeed, where any serious attempt has been made to heat the incoming gases or the intake manifold, the temperature attained by the air stream is almost invariably far higher than theoretically necessary. Improvement in vaporization should apparently be secured by better atomization, longer times of contact, or by throwing the unvaporized particles out of the insulating air stream onto a hot spot, rather than by raising the temperature of the mixture as a whole, with its attendant disadvantages.

With the same precautions as suggested above, raising the temperature of the intake manifold only slightly above present practice should make possible the utilization of fuels of considerably higher end-point, as far as completeness of vaporization and proper distribution are concerned.

It will be noted from the curve on Fig. 2 that the average boiling points of the equilibrium mixtures fall very close to the temperature at which 85 per cent of the original fuel has been boiled off, as indicated by the standard distillation curves. There is apparently some, though a not at all rigid, connection between these two points, for if, in each case, 135° C. be subtracted from the "85 per cent off" temperature, the result is a rough approximation (within 5° or 10° C.) to the initial condensation temperature of a 12 : 1 mixture at 1 atmosphere. This fact may serve as a means of estimating roughly the initial condensation temperatures of paraffin hydrocarbon fuels from a mere inspection of their distillation curves. The reason for this rather surprising relationship probably lies in the approximate equality of the heats of vaporization, and hence of the rate of change of vapor pressure with temperature, of the paraffin hydrocarbons. It would certainly *not* apply to fuels containing alcohol, benzene, etc.

Attention should also be called to the fact that the temperature at which the various original fuels exert a given vapor pressure is a comparative measure of the ease of starting in cold weather, provided there is sufficient priming. The minimum possible starting temperature is, however, probably 30° or 40° below the minimum temperature at which the fuel exerts a pressure sufficient to give a combustible mixture, because of the heating effect of the compression stroke before ignition.

---

[1] A. C. Fieldner, A. A. Straub and C. W. Jones, "Gasoline Losses Due to Incomplete Combustion in Motor Vehicles," This Journal, **13** (1921), 51; see also W. S. James, "Elements of Automobile Fuel Economy," read at Semi-Annual Meeting of the Society of Automotive Engineers, May 1921.

TABLE I SUMMARY OF PHYSICAL CONSTANTS OF THREE TYPICAL FUELS AND THEIR MIXTURES WITH AIR

FUEL	Average Boiling Point	Estimated Average Molecular Weight	Corresponding Formula	Specific Gravity at 20° C.	Degrees Baumé	Initial Boiling Point	50 Per cent Distilled	85 Per cent Distilled	End point	Initial Condensed from 12:1 Mixture	50 Per cent Condensed from 12:1 Mixture
Socony Motor Gasoline	128° C.	114	C_8H_{18}	0.743	60	60° C. 140° F.	128° C. 262° F.	169° C. 336° F.	211° C. 412° F.	40° C. 104° F.	2° C. 36° F.
High End-point Gasoline	147° C.	128	C_9H_{20}	0.752	57	62° C. 144° F.	154° C. 309° F.	208° C. 403° F.	252° C. 485° F.	63° C. 134° F.	9° C. 48° F.
Socony Kerosene	220° C.	170	$C_{12}H_{26}$	0.800	45	168° C. 334° F.	219° C. 426° F.	249° C. 480° F.	282° C. 539° F.	116° C. 242° F.	73° C. 163° F.

The vapor pressure curves for the partly condensed mixtures give an indication as to what can be accomplished as to starting in cold weather with various amounts of choking.

Table I compares the three fuels investigated in their more important characteristics.

It is hoped to continue this work further by determining the foregoing type of data for various types of blended fuels, naphthene base fuels, etc.

SUMMARY

This article may be briefly summarized as containing:

1—A new, simple, and reliable method for the determination of the temperatures of *initial* condensation of fuels from air-fuel mixtures.

2—An approximate method of determining the temperatures of *partial* condensation in air-fuel mixtures.

3—Vapor pressure data on three typical automotive fuels: Socony kerosene, Socony gasoline, and an artificially prepared high end-point gasoline.

4—A series of charts showing the condensation temperatures of these fuels under different conditions. These results show that the failure to obtain complete vaporization of present-day gasoline is due more to inefficient methods of securing vaporization than to any inherent limitation of the gasoline itself.

5—A suggested method for approximating roughly the initial condensation temperatures of paraffin hydrocarbon fuels from the distillation curves of these fuels.

6—A table of comparison of the more important characteristic properties of the fuels investigated.

ACKNOWLEDGMENT

The authors desire to express their appreciation to Dr. W. K. Lewis for his helpful suggestions in the course of the work, and to The Yale and Towne Manufacturing Company for their permission to publish that part of the work which was done at their expense.

The Total Sensible Heats of Motor Fuels and Their Mixtures with Air[1,2]

By Robert E. Wilson and D. P. Barnard, 4th

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS

OBJECT OF WORK

A feature which is of paramount importance to the efficient operation of an internal combustion engine, especially of the high-speed type used in motor cars, is that of securing a uniform mixture of fuel and air in the proper proportions before distribution to the cylinders. The only reasonably practicable way of accomplishing this seems to be in having the fuel nearly, or preferably completely, vaporized. In order to vaporize present commercial gasoline or any less volatile fuels completely, it is necessary to add some heat from external sources.[3] It is possible to secure satisfactory vaporization by any one or more of three methods, which may be classed as follows:

1—Atomization of cold fuel into heated air.

2—Atomization of cold fuel into cold air followed by heating the resulting mixture in the manifold. The "hot spot" aids vaporization partly by heating the mixture as a whole, but to a greater extent by throwing out the uncondensed drops onto the heated manifold surface and vaporizing the liquid directly.

3—Injection of the fuel as a superheated vapor into the cold air.

Methods 1 and 2 are frequently combined in the use of the hot spot together with a preheater. These first two methods suffer from a fundamental defect in that it has been found necessary, in order to vaporize the fuel completely in the short time available, to superheat the air or mixture considerably above its theoretical dew point. This results in decreased volumetric efficiency coupled with increased tendency toward knocking. Method 3, however, starts from the other side of equilibrium and is therefore theoretically the best means of securing the proper mixture, as it is necessary to heat the vaporized fuel only to such a temperature that the resulting mixture will be approximately at the dew point. Indeed, experimental results in this Laboratory and elsewhere have shown that the mixture prepared by this method may be as much as 30 to 35 per cent condensed before the distribution is seriously affected, because the extremely small particles formed by the rapid condensation of the superheated vapor do not tend to separate readily from the air stream. The particles thus produced are, at least for the first few moments after condensation begins, far smaller than those obtained by the best methods of atomizing a liquid.

The practical application of Method 3 requires fairly accurate data on two subjects—first, the dew points of various fuel-air mixtures; and, second, the specific heats, or rather, the total *sensible* heats, of fuels at high temperatures. The data on dew points have been covered in the preceding article. It is the purpose of this article, therefore, to cover the subject of specific and total sensible heats.

DATA IN LITERATURE

A survey of the available literature failed to yield any data on specific heats of paraffin hydrocarbons at the high temperatures required. Practically the only work done along these lines indicated that up to 100° C. the specific heat, averaged for a large number of petroleum distillates in the liquid state, could be fairly accurately represented by the equation:[1]

---

[1] Received July 27, 1921.

[2] Published as Contribution No. 37 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] See preceding article by the authors, "Condensation Temperatures of Gasoline- and Kerosene-Air Mixtures."

[1] Bushong and Knight, THIS JOURNAL, **12** (1920), 1197.

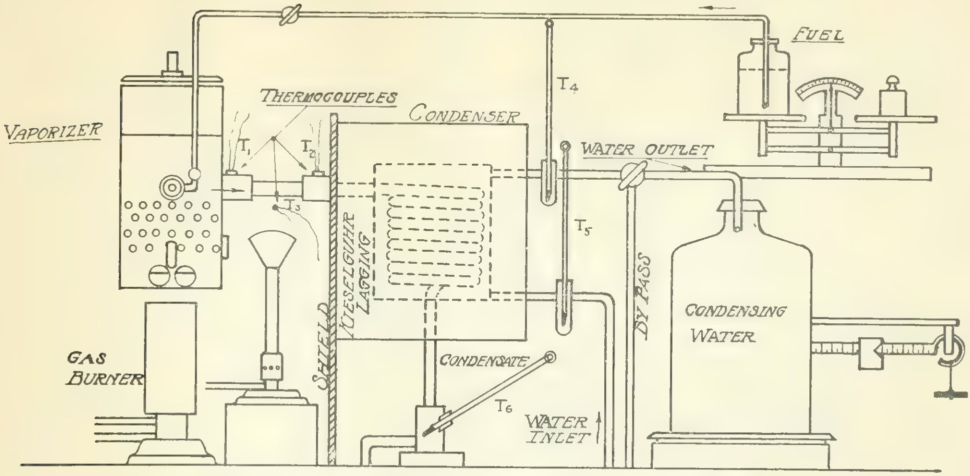


Fig. 1 Apparatus for Determining the Sensible Heats of Vaporized Fuels

$$Cp = 0.5 + 0.0008\ t$$

Other data [1,2,3] indicate that the specific heat at room temperature of light petroleum distillates is very close to 0.5. Such data as are available indicate, as do the vapor pressure curves (see preceding article), that the specific heats of the liquid and the vapor are substantially equal over the temperature range involved.

While the existing data on heats of vaporization of hydrocarbons are quite variable, as is shown by Table I, it is nevertheless possible by combining these data with Trouton's rule, which is known to hold quite well for hydrocarbons, to derive fairly satisfactory values for gasoline and kerosene.

For this work, the best values for the heats of vaporization were chosen as 60 cal. per g. for Socony kerosene (the average boiling point of which corresponds to dodecane) and 70 cal. per g. for Socony gasoline (average boiling point of which corresponds to octane). These figures represent a sufficiently good approximation for present purposes.

On account of the paucity of data at the higher temperatures, this Laboratory undertook to make some approximate experimental determinations of total sensible heats of two typical motor fuels up to about 500° C. The experimental method used in securing these data was probably not accurate to better than 3 or 4 per cent, but is sufficiently close to the truth for all practical work, especially in view of the rather indefinite composition of the materials investigated. The publication of the data appears worth while in view of the practical importance of the subject and the complete lack of any similar data in the literature.

Experimental Work

The experimental work was confined to two fuels: Socony kerosene and Socony motor gasoline, samples of which were very kindly furnished by the Boston branch of the Standard Oil Co. The gravity of the kerosene was 45° Bé., corresponding to a specific gravity of 0.800; and that of the gasoline was 60° Bé., corresponding to a specific gravity of 0.743. The same fuels were used in the previous vapor pressure work, and further data on them will be found in that article.

The total heats of these fuels were determined at various temperatures in the apparatus shown in Fig. 1. The distillate from the Rector vaporizer[1] was continuously condensed in a water-cooled steel coil. The condenser was tightly lagged with about 2 in. of kieselguhr, and the temperatures of the inflowing and outflowing cooling water were read from the thermometers T_4 and T_5. The cooling water was caught and weighed for each run. The weight of the cooling water multiplied by the difference in the temperatures T_4 and T_5 gave the heat given up by the fuel in cooling to the discharge temperature, T_6. The thermometers T_4 and T_5 were checked against each other, and showed no deviation over the range of temperatures involved. The vapor temperatures were measured by means of thermocouples placed at T_1 and T_2, and the air temperature (indicated by the thermocouple T_3) around the vapor pipe was kept slightly above that of the vapor in order to prevent more than minor heat losses. A variation of 75° to 100° C. in the air temperature produced

Table I—Heats of Vaporization of Hydrocarbons
(Calories per Gram)

Hexane C_6H_{14}	Heptane C_7H_{16}	Octane C_8H_{18}	Nonane C_9H_{20}	Decane $C_{10}H_{22}$	Undecane $C_{11}H_4$	Dodecane $C_{12}H_{26}$	Source
79.4	74.1	71.1	....	60.0	....	....	Maybery & Goldstein
....	....	63.54	63.1	62.0	....	60.0	Syniewski
....	(Aromatic Free Petrol) 74.0	....	....	....	....	(Kerosene) 60.0	Ricardo
81.6	74.5	71.5	67.5	64.5	61.4	59.0	Trouton's Rule $l = \frac{20.5\ T}{M}$
....	....	65.3	....	....	....	60.5	Wilson and Barnard[1]

[1] From slopes of vapor pressure curves (see preceding article).

---

[1] Maybery and Goldstein, *Am. Chem. J.*, **28** (1902), 28.

[2] H. E. Wales, "Specific Heats of California Petroleums," This Journal, **6** (1914), 727.

[3] V. Syniewski, *Z. angew. Chem.*, **1898**, 621.

[1] Kindly loaned for the purpose by the Yale and Towne Manufacturing Co.

TABLE II

FUEL	Run	Length of Run Min.	Heat Loss Correction	Q Determined	Q Corrected	Q — r	Temperature ° C.	r
Kerosene	1	12	24	336	360	300	460	60
	2	12	24	317	341	281	461	60
	3	12	24	317	341	281	459	60
	4	12	24	321	345	285	461	60
	5	10	20	265	285	225	375	60
	6	10	20	270	290	230	375	60
	7	10	20	262	282	222	365	60
	8	8	16	239	255	195	327	60
	9	8	16	233	249	189	318	60
	10	8	16	236	252	192	314	60
Gasoline	11	14	28	308	336	266	446	70
	12	14	28	300	328	258	434	70
	13	14	28	265	293	223	376	70
	14	12	24	242	266	196	338	70
	15	12	24	227	251	181	338	70
	16	12	24	235	259	189	340	70
	17	12	24	230	254	184	328	70
	18	8	16	202	218	148	290	70
	19	8	16	200	216	146	289	70
Kerosene	20	8	16	219	235	175	308	60
	21	8	16	230	246	186	308	60
	22	8	16	220	236	176	300	60
Water	23	20	40	756	797[1]	...	434	..
	24	20	40	757	798[1]	...	440	..

[1] From Marks and Davis' "Steam Tables" h at 434° C. $= \frac{1433}{1.8} = 797$ cal.

The difference between observed and above value = 798 — 757 = 41 cal. loss by radiation,, etc., per g. of fuel in 20 min.

no appreciable change in the vapor temperatures. There was at no time a difference of more than 5° or 6° C. between T_1 and T_2. As indicated in the drawing, the vaporizer was heated by means of a gas blast burner.

In making the determinations, the apparatus was allowed to run until substantially constant temperatures had been held at all points for at least 10 min. The time was then noted, and the condensing water was caught while 500 g. of fuel passed through the generator, readings being frequently taken to check the temperatures.[1] All runs were discarded in which the water temperatures varied over 1° C. In most cases the variation was less than 0.5° C. Several check runs were made at each temperature, the results of which are indicated in Fig. 2.

Since the condenser was admittedly not adiabatic, it seemed desirable to determine approximate figures for the heat losses and other correction factors by passing water through the generator and condenser, and comparing the total heat of the steam as thus determined with the very accurate values given in the Steam Tables.[2] The results were found to be 41 cal. per g. too low for 500 g. of water vaporized over a period of 20 min. The heat losses were therefore assumed to be 2 cal. per g. per min., and the results of the other determinations were subjected to this correction. This correction remains constant for all determinations, as the *same* weight of fuel was passed through in each case.

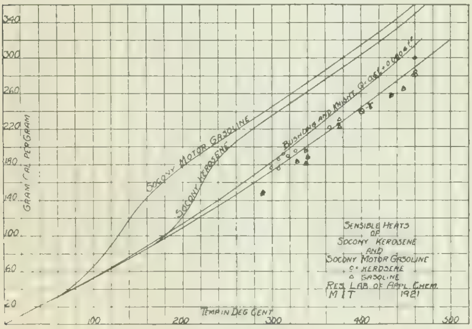


FIG. 2

RESULTS

The experimental results obtained by the foregoing procedure are recorded in Table II. The total sensible heats have all been corrected to 0° C.

It is very desirable to tie in these high temperature data with the values given in the literature for the specific heats of these hydrocarbons in the liquid state. This cannot be done indirectly, but by subtracting the value of r, the heat of vaporization of the fuel in question, from the observed figures for the total sensible heat at high temperatures, values may be obtained which should lie on a smooth curve with the data for the sensible heat of the liquids at temperatures below the boiling point.[1] The values thus obtained are presented in Column 7 of Table II, and graphically in Fig. 2. For the comparative purposes a line is drawn to represent the extrapolation of the recent data of Bushong and Knight[2] which were obtained from specific heat measurements on light petroleum distillate (liquid only) at temperatures up to 100° C. It will be noted that the agreement is not bad, considering the unjustifiable extrapolation of Bushong and Knight's equation:

$$\text{Specific heat} = 0.5 + 0.0008\, t, \text{ where } t = {}^\circ\text{C.}$$

The best representative line for the points determined in this Laboratory lies below the curve of Bushong and Knight and accords best with the equation:

$$\text{Specific heat (of either liquid or vapor)} = 0.5 + 0.0006\, t$$

It will be noted that values obtained for gasoline lie, on the average, about 5 cal. below the Q — r points for kerosene. This discrepancy, which is in the opposite direction from what might be expected, is very possibly due to the assumption of too large a value for the heat of vaporization for the gasoline. The value obtained from the slope of the vapor pressure curve of the identical fuel was, as indicated in Table II, 65.3 cal. per g., but a value of 70 was assumed in determining Q — r because it accorded better with other data in the literature.

Assuming, however, that the line Q — r is correct as drawn

---

[1] Although runs were made up to 460° C. there was no appreciable cracking in the short time that the gas occupied in passing through the system. This was indicated by the absence of any appreciable change in the distillation curve of the kerosene, and the fact that there was only a trace of noncondensible gas formed or of carbon deposited. Attempts to use a copper condenser gave trouble with cracking and the deposition of carbon.

[2] Marks and Davis, "Steam Tables and Diagrams."

[1] This method of treatment of the results is, of course, rigidly applicable only in cases where the heat of vaporization is substantially constant over the temperature range in question, and hence the specific heats of the liquid and the vapor are equal at a given temperature. That this is substantially true for the paraffin hydrocarbons in question is indicated both by data in the literature and by the fact that the vapor pressure data obtained by the writers for these fuels gave *straight lines* when log p was plotted against $\frac{1}{T}$.

[2] *Loc. cit.*

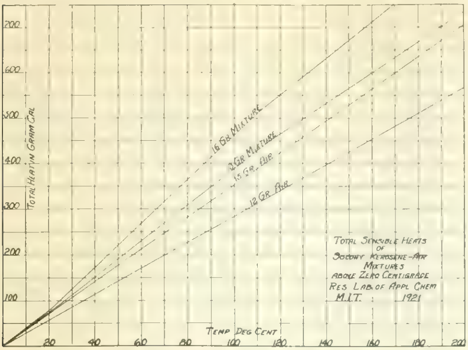


Fig. 3

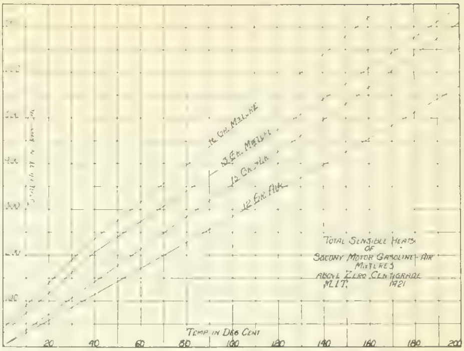


Fig. 4

for both fuels (since the divergence is just about within the limit of error of the method), it is then possible to add to this line the fractional amount of the heat of vaporization which corresponds to the fractional amount of the fuel which is vaporized at any given temperature. This was the method used in obtaining the curved lines shown in Fig. 2, which represent within a probable error of 3 or 4 per cent the values for the total sensible heats of gasoline and of kerosene as a function of temperature at a pressure of one atmosphere.

Figs. 3 and 4 give the sensible heats of kerosene-air and gasoline-air mixtures, respectively. The heats are given in gram calories for 13 g. and 16 g. of mixture, and also for 12 and 15 g. of air. The heat content of air was calculated from the equation:

$$H \text{ (per gram)} = \frac{6.5(T - 273) + 0.0005(T^2 - 273^2)}{29}$$

where H = heat in cal. per g.
T = temperature in degrees Kelvin (273 + °C.)

These curves make it possible to read directly the temperature of the resulting air-fuel mixture if the initial temperatures of the air and the fuel are known. If, for example, the fuel (kerosene) enters the mixing chamber at a temperature of 400° C., and the air at 50° C., then the total heat of 16 g. of a 15 : 1 mixture is equal to 304 + 175, or 479 cal. The final temperature of the resulting mixture corresponding to this heat content is 104° C.

By such calculations it is possible to determine just how hot the air or fuel should be heated before mixing in order to give a dry gas mixture at equilibrium, or indeed to determine any one of the three temperatures if the other two are known.

In this connection, there has been considerable speculation as to what happens with regard to the condensation or evaporation of the fuel during the compression cycle of an Otto cycle engine. The increase in pressure taken by itself would, of course, tend to cause condensation, but the heat liberated during the compression would raise the temperature of the mixture and tend to evaporate any uncondensed fuel. Without accurate data as to the change of vapor pressure with temperature and the sensible heat of a given fuel, it was impossible to give a definite answer to these questions, but, from data presented in this and in the previous paper by the writers, definite conclusions can be drawn as follows:

Making the calculations on a 5 : 1 compression ratio for Socony kerosene and assuming that the exponent k in the equation, pv^k = const., for the compression is 1.2 (which makes a maximum allowance for a cooling during compression), it can readily be shown that the tendency of the compression as a whole is to vaporize rather than condense the fuel, and indeed, that it would theoretically be possible to vaporize by compression a mixture of kerosene and air which was initially 75 per cent condensed. Actually, of course, the time would probably be insufficient to vaporize this amount of material, but it seems certain that if the mixture is nearly enough completely vaporized to give proper distribution, there will be very few, if any, liquid drops present at the moment of ignition, and that the fuel will, under no circumstances, condense out during compression.

Summary

This article describes certain approximate methods used by this Laboratory in determining the total sensible heat content of Socony motor gasoline and kerosene and their mixtures with air at temperatures up to 500° C. The resulting data are presented in such form as to make it readily possible to calculate, with sufficient accuracy for all practical purposes, the resultant temperature of an air-fuel mixture, knowing the temperature of the two constituents before mixing. Combined with data in a previous article on the dew points of various fuel-air mixtures, this information is very valuable in determining the proper conditions for securing a completely vaporized mixture of air and fuel in various types of carburetors and heated manifolds. The results also indicate that the net effect of the compression stroke on a motor is to vaporize, rather than condense, the fuel, and hence that the most difficult problem in connection with the vaporization of the fuel is to secure satisfactory *distribution*.

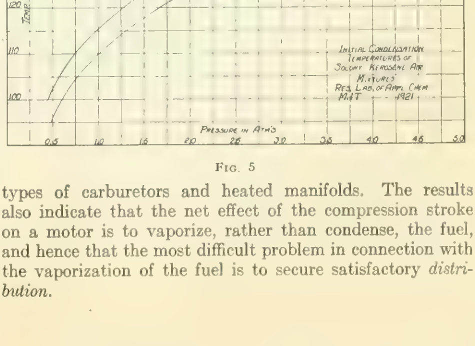


Fig. 5

Studies of Wheat Flour Grades. II—Buffer Action of Water Extracts[1,2]

By C. H. Bailey and Anna C. Peterson

Division of Agricultural Biochemistry, Minnesota Agricultural Experiment Station, St. Paul, Minnesota

Significance of H-Ion Concentration of Wheat Flour Doughs

Reaction is an important factor in controlling biological phenomena. All living tissues from the simplest to the most complex are affected by significant changes in the H-ion concentration of the fluids which bathe them. Bacteria, yeasts, and related microörganisms are no exception to this rule, and of late much attention has been given to the preparation of substrates with an optimum H-ion concentration for their culture and study. Sörenson[3] studied the influence of H-ion concentration on enzymatic activity and concluded that this can be controlled by adjusting the reaction. Clark[4] showed the effect of reaction upon the activity of bacteria and emphasized the necessity of employing culture media with the proper H-ion concentration. The studies of Euler and Emberg[5] establish the sensitivity of yeast and its enzymes to H-ion concentration. They found that the fermentation velocity, and the activity of invertase, reached a maximum in the vicinity of pH = 5.

Jessen-Hansen[6] concluded that there is a definite H-ion concentration to which the bread made from any particular wheat flour should best be brought. The optimum corresponds approximately to pH = 5.0; for choice flours it appears to be a little higher, and for poorer grades slightly lower. The same author later[7] suggests that "flour improvers" owe their value to the manner in which they increase the H-ion concentration of the dough.

Cohn and Henderson[8] state that the proper fermentation of bread dough is related to the increasing H-ion concentration, the dough being in best condition when a concentration is reached which turns methyl red from orange to red (about pH = 5.0). At this concentration the elasticity of gluten is at a maximum and the yeast most active; moreover, the development and activity of the organism causing "ropy" bread are depressed.

Observations made in this laboratory, as yet unpublished, show the isoelectric point of wheat gluten to be reached when the pH = 5.1 ±. It thus appears that the production of satisfactory yeast-leavened bread is best effected through a slightly acid condition of the dough. This acidity may result from the formation of organic acids by microörganisms, or by the deliberate addition of acid-reacting substances. Through the proper H-ion concentration the elasticity of the gluten, and the activity of the yeast and of "rope producing" bacteria are affected in the desired direction.

Significance of the Buffer Action of Flour

Jessen-Hansen indicated that the pH of high-grade wheat flours is numerically lower, *i. e.*, they have a higher H-ion concentration, than low-grade flours. This is in spite of the fact that the latter have a higher titrable acidity, the reason being the presence of more buffers in the lower grades. No data are presented in his paper, however, which establish in a definite manner the proportional relation between grade and buffer action. Since the variations in this regard are of significance in controlling the pH of doughs, it was deemed advisable to determine the magnitude of these differences. Such data would be of value in the preparation of doughs of any desired H-ion concentration by a definite, rather than a cut-and-try, process.

The Influence of Time and Temperature of Extraction upon the Buffer Action of the Extract

In developing a standard method of procedure a series of preliminary studies were conducted to determine the effect of time and temperature of extraction upon the buffer action of the extract. Two flours, a high-grade patent and a lower or second clear grade, were employed, in order to afford marked differences in the character and quality of material. A ratio of 1 part of flour to 5 parts of redistilled water was used in all of the determinations of buffer action. The water was first brought to the temperature used for extraction before adding it to the flour, which had also been brought to the same temperature. Extractions were made in water thermostats at 0°, 25°, 40°, and 60°, for periods of 1, 2, 4, and 6 hrs. The flour particles were kept in suspension by intermittent shaking during the extraction period. At the end of the period the flour particles were thrown out of suspension by whirling rapidly in a centrifuge for a few minutes. The clear decantate was divided into 100-cc. portions to which were added 10, 20, 30, 40, and 50 cc. of 0.02 *N* HCl, and like quantities of 0.02 *N* NaOH.[1] The H-ion concentrations of the original extracts and of the portions treated as described were then determined electrometrically by means of the hydrogen electrode described by Bailey,[2] connected through a calomel electrode to a potentiometer in the conventional manner. In addition, a number of colorimetric determinations were made, chiefly to ascertain the accuracy of this method. A later paper will detail certain of the observations made through the use of indicators. All of the data reported in the following tables and graphs were obtained by the electrometric method.

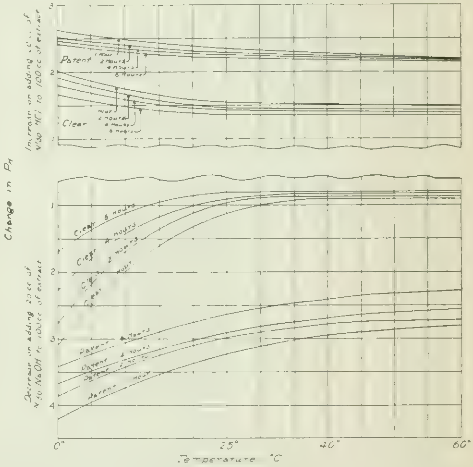


FIG. 1—RELATION OF TIME AND TEMPERATURE OF EXTRACTION TO THE BUFFER ACTION OF WATER EXTRACTS OF PATENT AND CLEAR FLOURS

Since the pH of the untreated extracts of the patent and of the clear flour was not affected by the time and temperature

---

[1] Received April 8, 1921.

[2] Published with the approval of the Director as Paper No. 216 Journal Series, Minnesota Agricultural Experiment Station.

[3] *Ergebnisse Physiol.*, **12** (1912), 393.

[4] *J. Infectious Diseases*, **17** (1915), 109.

[5] *Z. Biol.*, **69** (1919), 349.

[6] *Compt.-rend. trav. lab. Carlsberg*, **1** (1911), 170.

[7] *Z. ges. Getreidew.*, **4** (1912), 271.

[8] *Science*, **48** (n. s.) (1918), 501.

[1] In actual practice 25- or 50-cc. portions of the extract were used, together with proportional quantities of the 0.02 *N* HCl and NaOH.

[2] *J. Am. Chem. Soc.*, **42** (1920), 45.

TABLE I—INCREASES AND DECREASES IN H-ION CONCENTRATION (IN TERMS OF pH) RESULTING FROM THE ADDITION OF ACID AND ALKALI TO THE WATER EXTRACTS

Duration of Extraction Hours	Original Extract pH	Decrease in pH on Adding 0.02 *N* HCl					Increase in pH on Adding 0.02 *N* NaOH				
		0.02 *N* HCl per 100 Cc. Extract					0.02 *N* NaOH per 100 cc. Extract				
		10 Cc.	20 Cc.	30 Cc.	40 Cc.	50 Cc.	10 Cc.	20 Cc.	30 Cc.	40 Cc.	50 Cc.
					Patent Flour Extracted at 0°						
1	6.10	1.70	2.63	2.99	3.26	3.38	2.86	4.18	4.67	4.90	
2	6.09	1.56	2.51	2.95	3.17	3.33	2.08	3.85	4.46	4.76	4.97
4	6.10	1.54	2.45	2.89	3.12	3.29	1.68	3.67	4.21	4.74	4.94
6	6.09	1.51	2.40	2.84	3.11	3.27	1.59	3.41	4.22	4.66	4.92
					Patent Flour Extracted at 25°						
1	6.05	1.53	2.40	2.84	3.06	3.26	1.36	3.24	4.07	4.58	4.87
2	6.05	1.47	2.33	2.78	3.04	3.18	1.37	3.01	3.87	4.43	4.77
4	6.05	....	2.28	2.74	3.01	3.18	1.27	2.93	3.79	4.40	4.72
6	6.05	1.44	2.26	2.74	3.01	3.18	1.13	2.91	3.86	4.40	4.72
					Patent Flour Extracted at 40°						
1	6.00	1.49	2.35	2.77	3.04	3.20	1.52	2.61	3.94	4.47	....
2	6.02	1.47	2.33	2.76	3.02	3.21	1.23	....	3.79	4.33	4.67
4	5.99	1.40	2.20	2.71	3.01	3.18	1.06	2.48	3.45	4.12	4.51
6	5.99	1.37	2.20	2.69	3.01	3.17	1.06	2.45	3.43	4.00	....
					Patent Flour Extracted at 60°						
1	6.04	1.34	2.13	2.62	2.96	....	1.06	2.80	3.54	4.24	4.46
2	6.04	1.32	2.15	2.62	2.93	....	0.92	2.70	3.51	4.12	4.37
4	6.02	1.32	2.11	2.61	2.91	....	1.05	2.57	3.51	4.11	....
6	6.04	1.32	2.13	2.64	2.93	....	1.04	2.26	3.49	3.98	....
					Clear Flour Extracted at 0°						
1	6.29	1.20	2.01	2.63	3.03	3.25	1.47	3.08	3.92	4.36	4.62
2	6.29	1.17	1.93	2.57	2.94	3.21	1.20	2.75	3.65	4.20	4.28
4	6.29	1.07	1.81	2.42	2.84	3.21	0.95	2.26	3.23	3.80	4.19
6	6.27	0.98	1.67	2.28	2.72	3.02	0.78	1.69	2.88	3.43	3.99
					Clear Flour Extracted at 25°						
1	6.30	0.75	1.55	2.11	2.65	3.00	0.53	1.12	2.17	2.90	3.50
2	6.29	0.69	1.47	2.06	2.55	2.83	0.47	0.91	1.64	2.52	3.08
4	6.30	0.65	1.43	2.02	2.53	2.85	0.46	0.89	1.41	2.22	2.88
6	6.31	0.63	1.37	1.97	2.57	2.79	0.41	0.80	1.24	....	...
					Clear Flour Extracted at 40°						
1	6.29	0.69	1.51	2.10	2.54	2.87	0.47	0.90	1.54	2.50	3.11
2	6.30	0.67	1.47	2.06	2.51	2.85	0.43	0.85	1.39	2.22	2.98
4	6.30	0.64	1.41	2.04	2.51	....	0.40	0.82	1.38	2.15	2.78
6	6.30	0.65	1.40	1.98	2.40	2.72	0.41	0.80	1.24	....	....
					Clear Flour Extracted at 60°						
1	6.25	0.72	1.48	2.06	2.46	....	0.44	0.92	1.46	2.42	2.83
2	6.25	0.72	1.43	1.89	2.38	...	0.43	0.85	1.34	2.22	2.88
4	6.24	0.68	1.39	1.95	2.40	....	0.40	0.83	1.30	2.14	2.77
6	6.24	....	1.37	....	...	....	0.45	0.84	1.27	1.94	...

of extraction, the data secured are given in Table I in terms of the decrease and increase in pH effected by the progressive addition of acid and alkali, respectively. These show an increase in buffer action with an increase in time of extraction, and an even greater increase in buffer action when the temperature of extraction was elevated from 0° to 40°. The differences between the extract prepared at 40° and 60° are small. The changes in pH on addition of 20 cc. of 0.02 *N* HCl and 20 cc. of 0.2 *N* NaOH are shown graphically in Fig. 1.

EFFECT OF BOILING UPON BUFFER ACTION OF EXTRACT

The water extract of wheat flour contains a variety of complex substances, and the question arises as to which of these are responsible for the buffer action observed. Several proteins are usually present in such extract, notably leucosin (an albumin), gliadin (a prolamin), and some globulin. The leucosin is the typical water-soluble protein, and since it is coagulated by heat, an experiment was conducted to determine the effect of removing it by boiling. Portions of the original extracts prepared by shaking patent and clear flours with redistilled water at 25° for 1 hr. were immersed in boiling water for several minutes. After cooling, these preparations were made up to their original volume by replacing the water lost by evaporation. Their buffer action was then determined in comparison with the original extract which had not been heated. The results, given in Table II, show that the effect of thus coagulating the leucosin was slight, and that consequently it played an insignificant role in determining the buffer action of extracts in which it was present. It apparently functions to a small extent, however, as indicated by the fact that in the clear flour extract which contained the most soluble protein, the differences in buffer action between the original and the boiled extract were greatest.

Further, to verify the observations recorded in Table II, the buffer action of a series of flours of differing quality was compared with the soluble protein in the extract. The specific electrical conductivity of a 1 : 10 extract of these same flours had been previously determined by Bailey and Collatz.[1] These data will be found in Table III, and they appear to establish the fact that no relation exists between the percentage of protein in the extract and the buffer action of that extract as shown by the change in pH on addition of 20 cc. of 0.02 *N* NaOH to 100 cc. of the extract. The buffer action increases regularly with the electrical conductivity, however, which suggests that the buffers may be chiefly electrolytes. A study of phytase by Collatz and Bailey[1] showed that enzyme to respond to variations in temperature in hydrolyzing phytin, as evidenced by the rate of change in electrical conductivity of phytin-phytase solutions. A similar response in terms of buffer action to variations in the conditions of extraction has been shown in Table I. These facts suggest that the buffer action of flour extracts is probably due in large part to phosphates produced from phytin through the action of phytase during the period of extraction with water.

TABLE II—COMPARISON OF THE BUFFER ACTION OF THE ORIGINAL AND BOILED EXTRACTS OF PATENT AND CLEAR FLOURS

TREATMENT	H-Ion Concentration Not Boiled pH	Boiled pH	Difference pH
Patent flour extracts			
Original extract of patent flour..........	6.05	6.07	0.02
100 cc. extract + 20 cc. 0.02 *N* HCl......	3.68	3.65	0.03
100 cc. extract + 20 cc. 0.02 *N* NaOH...	9.28	9.35	0.07
100 cc. extract + 40 cc. 0.02 *N* NaOH...	10.62	10.67	0.05
Clear flour extracts			
Original extract of clear flour.............	6.32	6.37	0.05
100 cc. extract + 20 cc. 0.02 *N* HCl......	4.75	4.61	0.14
100 cc. extract + 20 cc. 0.02 *N* NaOH...	7.42	7.66	0.24
100 cc. extract + 40 cc. 0.02 *N* NaOH...	9.21	9.53	0.32

TABLE III—THE BUFFER ACTION, ELECTRICAL CONDUCTIVITY, ASH, AND WATER-SOLUBLE PROTEIN CONTENT OF A SERIES OF FLOURS

SAMPLE	Ash Per cent	Specific Conductivity $K_{30^\circ} \times 10^{-4}$	Increase in pH on Adding 20 Cc. 0.02 *N* NaOH to 100 Cc. Extract	Soluble Proteins Per cent
First middling ...	0.44	5.36	3.21	1.26
Second middlings .	0.45	5.49	2.62	1.45
Third middlings ..	0.55	6.26	2.37	1.57
Second break.....	0.58	6.67	2.27	1.40
Fifth middlings...	0.61	6.69	2.07	1.35
Third break.	0.67	7.59	1.67	1.59
Fourth middlings .	1.17	10.00	0.87	2.45
First break.......	1.34	11.24	0.83	2.09
Fourth break.....	1.62	12.18	0.72	2.09

---

[1] THIS JOURNAL, **13** (1921), 319.

[1] THIS JOURNAL, **13** (1921), 317.

TABLE IV—H-ION CONCENTRATION AFTER ADDITION OF ACID AND ALKALI TO THE EXTRACT OF FLOURS OF DIFFERENT GRADES

		0.02 N HCl Added per 100 Cc. Extract					0.02 N NaOH Added per 100 Cc. Extract			
Flour Grade	Ash Per cent	40 Cc. pH	30 Cc. pH	20 Cc. pH	10 Cc. pH	Original Extract pH	10 Cc. pH	20 Cc. pH	30 Cc. pH	40 Cc. pH
Patent[1]	0.40	3.01	3.25	3.72	4.55	6.02	7.69	9.40	10.41	10.82
1st middlings	0.44	2.87	3.11	3.60	4.48	6.07	7.47	9.28	9.89	10.62
2nd middlings	0.45	2.96	3.25	3.64	4.65	6.10	7.27	8.72	9.79	10.32
3rd middlings	0.55	3.04	3.45	3.96	4.94	6.22	7.22	8.59	10.00	10.35
2nd break	0.58	3.15	3.45	4.11	5.00	6.25	7.12	8.52	9.53	10.21
5th middlings	0.61	3.16	3.53	4.14	5.04	6.31	7.15	8.38	9.62	10.22
3rd break	0.67	3.46	3.62	4.18	5.19	6.22	6.96	7.89	9.25	9.77
1st clear[1]	0.83	3.48	3.96	4.60	5.49	6.40	6.97	7.64	8.81	9.62
4th middlings	1.17	4.06	4.46	5.11	5.85	6.42	6.86	7.29	7.91	8.79
1st break	1.34	4.04	4.56	5.15	5.86	6.34	6.77	7.17	7.66	8.59
2nd break	2.38	4.80	5.26	5.73	6.12	6.44	6.73	7.02	7.27	7.66

[1] Flours from Mill C. All others from Mill A.

THE RELATION OF BUFFER ACTION TO THE GRADE OF FLOUR

The grade of wheat flour is quite definitely related to the percentage of ash which it contains, and the ash determination is extensively employed in commercially estimating the grade of flour. The data reported in Tables I and III indicate a parallelism between ash content, flour grade, and the buffer action of flour extracts. To verify this parallelism further, the series of flours employed by Bailey and Collatz, in studying the specific conductivity of water extracts, were extracted with water at 25° for 1 hr., and the buffer action of the extracts determined. In Table IV, the results are arranged in order of the ash content of the flour. Since the pH of the original extracts of the several flours varies, the actual, rather than the change in, pH is here recorded. It will be observed that as the ash content increases, and the grade diminishes, the buffer action of the extracts increases. Consequently, it requires appreciably more hydrochloric acid to change the pH of the lower grades through a given range than it does in case of the patents. The best index to the flour grade is afforded by the extracts to 100 cc. of which 20 cc. of 0.02 N NaOH were added. In Column 9 of Table IV, where these data are recorded, it will be observed that the pH of the extract so treated diminishes regularly with the increase in ash content. Fig. 2 shows graphically the electrometric titration curves of five characteristic flours of different ash content selected from the several reported in Table IV.

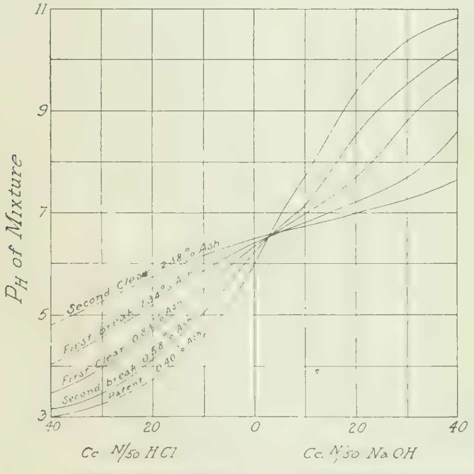


FIG. 2—ELECTROMETRIC TITRATION CURVES OF WATER EXTRACTS OF FIVE TYPICAL FLOURS REPRESENTING DIFFERENT GRADES

In view of the decided differences in the buffer action of high-grade or patent, and low-grade or clear flours, it is possible that some of the difficulties experienced in producing satisfactory yeast-leavened bread from the lower grades may be due to failure to obtain the proper H-ion concentration of the dough. Further experimentation with these lower grades of wheat flour, containing more than 0.60 per cent of ash, should be conducted to ascertain the possibilities in this direction. Since conditions generally are unfavorable to the production of choice bread from clear flour, it is probable that a more careful adjustment, within narrower limits, is necessary than in case of doughs made from patent flour.

SUMMARY

1—Varying the time and temperature of extraction does not appreciably alter the H-ion concentration of the extract. The buffer action of such extracts is, however, increased somewhat with increased time of extraction, and quite appreciably increased as the temperature during extraction is increased from 0° to 40°.

2—Boiling the extract reduces its buffer action very slightly, indicating that the soluble proteins which coagulate on boiling are not the principle buffers of the extract. A lack of correlation of the buffer action of extracts of several flours with the percentage of soluble proteins in the extracts further confirms the belief that the proteins are not chiefly responsible for the buffer action.

3—Since the buffer action parallels the specific conductivity of water extracts, and varies with modified conditions of extraction in the same direction and to about the same degree as the activity of phytase varies in hydrolyzing phytin, it appears that phosphates, produced by the hydrolysis of phytin by phytase during extraction with water, may be the principal buffers in the extract.

4—Electrometric titration curves show the extracts of high-grade flours to be buffered less than the extracts of lower grades. It consequently requires less acid to bring the H-ion concentration of a high-grade or patent flour dough to the optimum for bread production than is required for a low grade flour. Possibly some of the difficulties experienced in making satisfactory bread from the lower grade or clear flours may be due to failure to obtain the optimum H-ion concentration of the dough.

Copper and Brass Research Association

The formation of the Copper & Brass Research Association an unincorporated, voluntary organization of the copper, brass, and copper alloy interests, was recently announced by its president, R. L. Agassiz, also president of the Calumet & Hecla Mining Co. The purpose of the Association, given in its by-laws, is to stimulate coöperative effort in the use of copper, brass, and copper alloy products. Membership in the Association is open to producers of copper sold here or selling agents of copper in the United States; to fabricators of copper, brass, and copper products generally in the United States and Dominion of Canada, and to others directly engaged in, or connected with the copper and brass industries. The following are the officers of the Association: R. L. Agassiz, *president;* Fred S. Chase and C. F. Kelley, *vice presidents;* Stephen Birch, *treasurer;* W. S. Eckert, *secretary.* Mr. William A. Willis has been appointed manager of the Association, which has offices in New York City.

Grape-Seed Oil[1]

By **Frank Rabak**

Bureau of Plant Industry, U. S. Department of Agriculture, Washington, D. C.

In the grape juice industry of the United States there results annually, as a by-product, approximately 1100 tons of grape seeds. These seeds are at the present time entirely wasted, probably because of lack of knowledge regarding the proper methods of converting them into products of value.

The utilization of these seeds, largely for the oil they contain, has long been under consideration in foreign countries where the seeds result as by-products of the wine industry.

Probably the first mention of grape-seed oil as a possible industry was in 1780 when, according to Marre[2] in a report addressed to the Chamber of Commerce of Nimes, M. Claude Lorrain called attention to the erection at Albi of a factory for the exclusive extraction of the oil. From this time on much has been published on the subject.[3]

Within the last decade, Fachini and Dorta[4] have reported on several oils extracted by different methods from Italian grapes. The following year Marre[5] stated that in four French departments, namely, Gard, Herault, Aude, and Pyrenees-Orientales, there were available 1,036,000 hundredweight of seeds, which on a basis of 15 per cent of oil would yield 155,000 hundredweight of oil. The oil was said to compare favorably with second-class olive oil for food purposes. Paris[6] likewise called attention to the large amount of grape seeds wasted in Italy, stating that if the seeds from the wine industry were utilized there would be sufficient quantity to yield 18,000 liters of oil annually. Grape-seed oil is an important product of the wine regions of France and Italy, according to a report[7] which stated that the oil was obtained by either hot or cold pressure or by the use of solvents. The oil was mentioned as being useful as an edible oil or in the manufacture of soap. The composition of the oil from the standpoint of its use in the manufacture of varnishes has also been reported.[8] In a report by Wilson[9] in 1913, it was stated that the newspaper *La Cronica Meridional*, Almeria, Spain, called attention to the production of grape-seed oil, stating that, taking 10 per cent as the average yield, 1 kilo (2.2 lbs.) of oil could be obtained for each hectoliter (26.42 gals.) of wine.

In 1913 Darner[10] reported the properties of an oil extracted from California grapes. Dellacqua[11] showed the similarity in composition of grape oil and soy and maize oils.

While the oil has received attention largely in Europe, Dawson[12] recently reported similar activities in South America, stating that a Rosario, Argentina, soap and chemical manufacturer had obtained an exclusive concession from the province of Mendoza for 10 years for the exploitation of the industry. It was stated that a plant with a capacity of 550,000 to 650,000 lbs. of oil a year would be established to utilize the grape seeds from the wine industry.

In connection with the campaign for oils from various sources in Germany during the war, Meyer[1] called attention to the extraction of oil from the seeds of wine grapes, which yielded 10 per cent oil by extraction with benzene. Uflerbaumer[2] also mentioned grape seeds as a valuable source for oil to alleviate war conditions in Germany, Austria, and Hungary, stating that these countries could produce 1,080,000, 2,000,000, and 1,770,000 kilos of oil, respectively. The methods of pressing, extracting and refining grape-seed oil from wine residues in Germany were given in a report by N. and H.[3] More recently Ventre[4] in 1918 and Rothea[5] in 1919 have called attention to the possibility of oil extraction from grape seeds in France. The properties and commercial uses of the oil have also been discussed by Klinger.[6]

SOURCE OF AMERICAN OIL

The principal variety of grapes grown for the manufacture of grape juice in the United States is the commonly known Concord. The seeds from these grapes have been found to contain varying quantities of fatty oil, the variation being probably related to conditions of ripeness. The average yield of oil from the clean dry seeds is about 13 per cent.

EXTRACTION OF OIL

PRESSURE—The oil may be obtained by two methods, namely, by pressure and by solvent extraction. The most efficient method for extracting the oil by pressure is by means of the expeller type of press. On account of the comparatively low percentage of oil in the seeds, it is necessary, when this method is employed, to decorticate the seeds in order to eliminate a large proportion of non-oil-yielding hulls (about 44 per cent). The percentage of oil in the remaining kernels is increased considerably by this treatment, enabling the latter to be passed through the press and extracted efficiently. The yield of oil obtained by this process from the decorticated seeds was 14.5 per cent.

SOLVENT EXTRACTION—Solvent extraction is best accomplished by means of benzene. While oil extracted by benzene contains more impurities than that obtained by pressure, it apparently submits to refining, but with a somewhat greater refining loss. Since the pressure method is probably the most practical for complete utilization of the seeds, because of the fact that the press cake remaining is more satisfactory as a stock food, only the pressed oil will be considered in this investigation.

REFINING OF OIL—The crude oil obtained by pressure was deep yellowish green in color, and possessed a decided, nutlike, slightly burnt odor and taste. This oil was treated with about 8 per cent of fuller's earth, filtered, and subjected to steam distillation for several hours. The resulting bleached and deodorized oil (which will be referred to as a refined oil) possessed a pale straw color and a bland, sweetish, nutlike taste, and was practically odorless.

---

[1] Received April 25, 1921.

[2] *Rev. gen. chim.*, **14** (1911), 186.

[3] J Fontenele, *J. chim. med.*, **3** (1827), 66; G. Schübler, *J. tech. okonom. Chem.* **2** (1828), 364; **5** (1829), 31; Minutoli, *Ibid.*, **10** (1831), 352; *Dinglers polytech. J.*, **148** (1858), 238; A. Fitz, *Ber.*, **4** (1871), 442; *Sci. American*, **57** (1887), 241; J. Jobst, *Gewerbeblatt aus Württemberg*, **37** (1885), 44; De Negri and Fabris, *J. Soc. Chem. Ind.*, **12** (1893), 606*a* (original article, *Ann. Chim. Centr. Gabelli*, **1891–1892**, 225, not seen); F. M. Horn, *Mitt. kgl. Techn. Gewerbe-Mus.*, **1** (1891), 185; *Chem. Rev. Fett Harz-Ind.*, **10** (1903), 219; Ulzer and Zumpfe, *Oesterr. Chem.-Ztg.*, **8** (1905), 121.

[4] *J. Soc. Chem. Ind.*, **29** (1910), 1019. (Original article, *Ind. chim. min. met.*, **10** (1910), 183, not seen.)

[5] *Loc. cit.*

[6] *Staz. sper. agrar. ital.*, **44** (1911–1912), 669.

[7] *Pure Products*, **8** (1912), 217.

[8] K. P., *C. A.*, **7** (1913), 3246. (Original article, *Seifenfabr.*, **33** (1913), 719, not seen.)

[9] *Daily Consular & Trade Reports*, 16th year, Jan. 2, 1913, No. 1, 27.

[10] N. Dakota Station, *Special Bulletin* **21** (1913), 370.

[11] *Ann. chim. applicata*, **2** (1914), 295.

[12] *Commerce Reports, Daily Consular & Trade Reports*, No. 18, Jan. 22, 1915, 317.

[1] *Apoth.-Ztg.*, **30** (1915), 595.

[2] *Chem. Umschau Fette, Oele, Wachse Harze*, **23** (1916), 20.

[3] *C. A.*, **11** (1917), 1322. (Original article, *Z. angew. Chem.*, **29** (1916), **1**, 337, not seen.)

[4] "Exploitation et utilization des Pepins de Raisins," *Prog. agr. vit.*, **39** (1918), 31, 54, 80.

[5] *Bull. sci. Pharmacol.*, **26** (1919), 105.

[6] *Farben-Ztg.*, **26** (1920), 6.

Table I—Physical and Chemical Constants of Grape-Seed Oil from Foreign and Domestic Grapes

	Domestic Oils		Foreign Oils						
Physical and Chemical Constants	Crude	Refined	Horn	Fachini and Dorta	Rothea	De Negri and Fabris	Ulzer and Zumpfe	Fabris and Settimj	Klinger
Color	Deep yellowish green	Pale straw	....	....	....	Bright yellow	....	....	Bright yellow
Odor	Nutlike, charry	Faint, pleasant	....	....	....	Rancid	....	....	Pleasant, grape-like
Taste	Fatty, nutlike, slightly bitter	Fatty, nutlike, agreeable	....	....	....	Rancid	....	....	....
Specific gravity	0.9208 at 25° C.	0.9204 at 25° C.	0.9561 at 15° C.	0.9262 at 15° C.	0.9261 at 15° C.	0.935 at 15° C.	0.9215 at 15° C.	0.925 at 15° C.	0.925
Index of refraction	1.4720 at 25° C.	1.4720 at 25° C.	....	....	1.4760	....	1.4713 at 25° C.	....	....
Congealing point	—19 to —21° C.	—22 to —24° C.	—10 to —12° C.	....	....	—10 to —13° C.	....	—13° C.	....
Acid value	1 21	0.74	16.2	7.9	14.1	....	....	....	....
Saponification value	193.4	192.2	178.4	189.7	195.3	178.5	190.0	178.3	192.0
Iodine value	134.1	135.8	94 0	129.4	129.0	95.8	142.8	130.3	130.9

PHYSICAL AND CHEMICAL PROPERTIES OF CRUDE AND REFINED OILS

In order to make a comparison of the general physical and chemical properties of the oils with grape-seed oils of foreign origin the tabulation in Table I was made.

It will be noted from this table that the physical and chemical properties of grape-seed oil reported by foreign investigators differ in many respects from those of the domestic oils. The specific gravities of the several foreign oils differ considerably among themselves, although all are recorded as observed at the same temperature. They also differ materially in this respect from the domestic oils. Likewise, the congealing point of the foreign oils is considerably lower. In acid value, there is much variation, probably due to the methods of extraction and the condition of the seeds before extraction. The saponification and iodine values recorded by Fachini and Dorta, Rothea, Ulzer and Zumpfe, and Klinger correspond fairly closely with those obtained for domestic oils. The unusually low iodine values of Horn and De Negri and Fabris are difficult to explain.

CHEMICAL EXAMINATION OF THE REFINED OIL

Determinations of the volatile acids (Reichert-Meissl value), soluble acids, insoluble acids (Hehner value), acetyl value, and unsaponifiable were made according to the methods recommended by Association of Official Agricultural Chemists.

Examination showed that 0.47 per cent of the oil consisted of volatile acids. There was an entire absence of soluble acids. The amount of insoluble acids (Hehner value) in the oil was 94.75 per cent. The acetyl value was 9.89, and the amount of unsaponifiable was 1.61 per cent.

The insoluble acids obtained from the oil were separated into the solid and liquid acids by the lead-ether method, as recommended by the Association of Official Agricultural Chemists.

The physical and chemical characteristics of the insoluble acids, and the solid and liquid acids, together with the yields obtained, are included in Table II.

Table II—Physical and Chemical Properties and Yields of Insoluble, Solid and Liquid Acids of Grape-Seed Oil

Yields and Physical and Chemical Properties	Insoluble Acids	Solid Acids	Liquid Acids
Yield, per cent	94.75	7.17	85.41
Color	Dark, golden yellow	White, brittle, waxy	Golden yellow
Odor	Strongly fatty	None	Pleasant, fatty
Taste	Fatty, sweetish, bitter	Waxy	Sweetish, fatty
Specific gravity at 25° C.	0.9047	....	0.9080
Index of refraction at 25° C.	1.4637	....	1.4652
Congealing point	+10° to +9° C.	....	—7.5° to —9° C.
Melting point	....	53.5° to 54.5° C.	....
Neutralization value	194.9	212.1	192.9
Mean molecular weight	287.8	264.5	290.8
Iodine value	137.0	....	144.7

SOLID ACIDS—The solid acids, with a neutralization value of 212.1, probably consist of palmitic and stearic acids with a preponderance of the former, since the neutralization values of these acids in pure condition are 219.1 and 197.5, respectively.

From the neutralization value the mean molecular weight of the solid acids was found to be 264.5. The molecular weights of pure palmitic and stearic acids are 256 and 284, respectively. Using the mean molecular weight 264.5 as a basis for calculation, the respective proportions of these acids, according to the method of Lewkowitsch,[1] were found to be 69.64 per cent palmitic and 30.36 per cent stearic acid. These percentages represent the proportion of the acids in the mixed solid acids. The percentage of these acids in the original oil, which consisted of 7.17 per cent solid acids, was found to be 4.99 per cent palmitic and 2.17 per cent stearic acid.

Reducing the above percentages of palmitic and stearic to terms of the glycerides, palmitin and stearin, in which form these acids occur in the oil, it was found that grape-seed oil consists of 5.23 per cent palmitin and 2.26 per cent stearin.

LIQUID ACIDS—A comparison of the physical and chemical properties of the liquid acids indicates a mixture of oleic and linoleic acids. Oleic acid is indicated by the specific gravity, refraction, and neutralization value, while linoleic acid is indicated by the comparatively high iodine value of the mixed acids, which is 144.7. Using this latter figure as a basis for calculation according to the method of Lewkowitsch,[2] it was found that the liquid acids consist of 59.8 per cent of linoleic acid and 40.2 per cent of oleic acid. Since the original oil consisted of 85.41 per cent of liquid acids, it is found from the above percentages of these two respective acids that the oil consists of 51.27 per cent linoleic acid and 34.33 per cent oleic acid. These acids are combined in the oil in the form of the glycerides, linolein and olein. When the percentages of the acids were expressed in terms of their glycerides, the oil contained approximately 53.59 per cent linolein and 35.87 per cent olein.

SUMMARY

Domestic grape-seed oil as obtained from the Concord grape possesses some properties comparable with oils of foreign origin. The differences noted may be ascribed to conditions of growth, climate, soil, variety, and methods of extraction. It is highly probable that the oils from domestic grapes of a single variety would exhibit slight differences in their properties due to seasonal variations.

The results of the examination of grape-seed oil indicate the following approximate composition:

	Per cent
Linolein	53.59
Olein	35.87
Palmitin	5 23
Stearin	2.26
Unsaponifiable matter	1.61

---

[1] 10th Ed., I, 515.

[2] *Ibid.*, 457.

The remainder of the oil consists of small amounts of free fatty acids and volatile fatty acids.

On account of its ease of refining, grape-seed oil should find its most important commercial use as an edible or condimental oil. Its application as a drying oil is also indicated by its comparatively high iodine value, which places it in the semi-drying class of fatty oils.

In view of the comparative ease of extraction of the oil the utilization of the waste seeds from the grape juice industry of the United States for the production of an edible oil is recommended.

The Effect of Some Decolorizing Carbons upon the Color and Colloids of Cane Juice[1,2]

By Joseph F. Brewster and William G. Raines, Jr.

Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., and Louisiana Sugar Experiment Station, New Orleans, La

Previous investigations at the Louisiana Sugar Experiment Station, the results of which have been published chiefly by Zerban and his co-workers, have demonstrated that filtration of cane juice with the aid of kieselguhr, followed by filtration with active decolorizing carbon, is greatly superior to the older sulfur-lime method of clarification in removing color and other impurities from the juice. The kieselguhr-carbon filtration process was given a trial on a large scale in Louisiana during the past grinding season, and reports indicate that it cannot yet be regarded as a commercial success, although sugar and molasses of excellent quality were produced directly from juice. The chief factor to be considered in explaining why the new process may not yet be successful is the cost of filtering materials, and probably also the costs involved in working the process, as compared with the cheap materials and the low costs of operating the older processes. The chief use of highly activated decolorizing carbons in the sugar industry will probably be confined for the present to the refining of raws.

In view of the above facts, and in consideration of the huge quantities of waste vegetable materials available for the manufacture of decolorizing carbons, it is natural that much interest has been created in the manufacture and uses of such carbons, and we think the belief is justified that high-grade carbons at low cost will be produced in the near future. The subject of the preparation of vegetable decolorizing carbons from various raw materials has been treated in one of the Louisiana Sugar Station's bulletins by Zerban, Freeland and Sullivant.[3]

Up to the present very few decolorizing carbons are being produced on a large scale. Several carbons are being developed in this country, however, and at the suggestion of Mr. Paine of the Carbohydrates Laboratory, Bureau of Chemistry, it was decided to test as many of these as possible in the Station's sugar house. Four such carbons were obtained.[4]

THEORETICAL CONSIDERATIONS

Schneller[5] demonstrated the presence of polyphenols in various parts of the sugar cane by means of the well-known color reaction which these give with salts of iron. He concluded that the polyphenols, expressed with the juice and coming in contact with iron already present in the cane or dissolved from rolls, piping, and other sugar house equipment, cause discoloration of the juice. Schneller also pointed out that the polyphenol-iron compounds are only temporarily bleached by sulfur dioxide and reappear on neutralizing.

Zerban[1] has studied some of the coloring matters of cane and has found that, in the methods of clarification generally practiced in Louisiana, the dark color in cane products appears to be due almost entirely to polyphenol derivatives occurring in cane juice, the color being two to three times as dark when ferric salts are present with the polyphenols. He also points out that under certain conditions the natural coloring matters of cane, anthocyanin and saccharetin, which are polyphenol derivatives, may contribute materially to the color of the juice.

It was found by Zerban and Freeland[2] that decolorizing carbons will remove practically all the color from cane juice, as well as the polyphenols, the iron combined with them, and substances which under certain conditions are capable of producing polyphenols.

In connection with the purification of cane juice there must be taken into consideration the presence of other impurities aside from those which are responsible for color; namely, impurities which exist in the colloidal state. Schneller,[3] and later Zerban,[4] called attention to this subject, and the latter, with others, is of the opinion that cane-juice clarification, whether accomplished by so-called chemical means or by the use of adsorbents such as kieselguhr and carbon, is to be regarded as a colloid-chemical proposition.

The impurities of cane juice from the rolls may be considered to exist in all degrees of dispersion. The gross impurities, such as soil particles, finely ground bagasse, etc., are visible to the eye. Some of these may be thrown down by centrifuging, but the liquid will still be opaque. If the centrifuged juice be poured upon a paper filter, some of the suspended matter will first pass through. As the pores of the paper become clogged the liquid will pass through clear, but by this time filtration will have become very slow. If, however, the raw juice is brought to boiling with about 2 per cent of its weight of kieselguhr, filtration is rapid, and the filtrate is brilliant and clear, although colored. If juice thus clarified be completely dialyzed and the dialysate evaporated to dryness, there will be found a solid residue which sometimes has a gelatinous appearance and often is nearly colorless. This residue contains both organic and inorganic material, as is shown by ashing. In dialyzing cane juice it has been noticed that a great deal of the coloring matter will pass through a collodion membrane, some of the color being adsorbed in the membrane itself.

Paine and Walton[5] made use of the dialysis method in comparing the efficiency of different kinds of kieselguhr, and it is at their suggestion that this method has been used for a part of the work reported here.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] The matter described in this paper is the result of coöperation between the Bureau of Chemistry, United States Department of Agriculture, and the Louisiana Sugar Experiment Station. The work was done at the Station's sugar house and laboratory at New Orleans during the cane grinding season of 1920–21, and the authors desire here to express their appreciation and thanks to Mr. W. G. Taggart, assistant director of the Sugar Station, who, by helpful suggestions and actual labor, enabled them to obtain the results described herein.

[3] *Bulletin* **167** (May 1919).

[4] We owe our thanks to the National Carbon Co., of Cleveland, and to Dr. J. W. Turrentine, Bureau of Soils, U. S. Department of Agriculture, in charge of the potash plant of the Department at Summerland, Cal., for supplying us with 100-lb. lots of their carbons.

[5] Louisiana *Bulletin* **157** (August 1916).

[1] THIS JOURNAL, **12** (1920), 744.

[2] Louisiana *Bulletin* **165** (March 1919).

[3] *Louisiana Planter*, **56** (1916), 44.

[4] Louisiana *Bulletin* **173** (March 1920).

[5] *Science*, **53** (1921), 266.

The colloids of cane juice have proved an abomination to the sugar manufacturer. They are thought to cause frothing during evaporation, and then often flocculate and precipitate in the sirup. They retard crystallization, and adhere to the sugar after it has been centrifuged, acting as a binder for coloring matter and forming a film on the sugar crystal which retains moisture, thus offering a favorable medium for the growth of molds and bacteria which brings about decomposition of the sucrose when the sugar is stored. To the sirup maker, on the other hand, the colloids may be regarded as being useful, in that they retard crystallization.

Sugar House and Laboratory Results

SULFUR-LIME PROCESS—For the sake of comparison with the kieselguhr-carbon process by the dialysis method, three runs by the sulfur-lime process are recorded. These runs were made in the usual way, on about 3000 lbs. of juice each, by sulfuring to 5-cc. acidity and liming back to 0.5 cc. Samples of raw, sulfured, and limed juice, respectively, were dialyzed. Each 200-cc. sample of juice, after mixing with a little toluene, was poured into a collodion sack of about 1000-cc. capacity and dialyzed, first in running tap water, then in four daily changes of distilled water. After dialysis, the contents of the sack were transferred and evaporated to dryness on the water bath, heated at 110° for 15 hrs., and weighed. This gave total nondialyzable solids. The residues were then washed and reweighed.

The results of this treatment are shown in Table I, expressed as mg. of nondialyzable solids and ash per 100 cc. of juice. No corrections have been made for change in specific gravity, as this was found to have little effect upon the figures.

Table I—Sulfur-Lime Clarification

Run	Solids Raw	Solids Sulfured	Solids Limed	Ash Raw	Ash Sulfured	Ash Limed
1	366.6	50.1	38.7	11.5	13.3	13.4
2	483.8	44.8	52.3	22.8	15.0	17.2
3	407.1	70.3	51.1	40.4	28.1	21.7

The significant figures of Table I are those of the juice after liming, since the impurities remaining at this stage of the treatment are carried through the following steps of evaporation and boiling. In Runs 1 and 3 there is considerable reduction in the amount of colloids by liming, while in Run 2 there is an increase. This increase is probably due to over-liming, it being well known that a part of the precipitate brought down by sulfur dioxide may be redissolved on liming back. No color determinations were made in connection with the sulfur-lime runs.

It is interesting to compare the quantity of colloids remaining in the juice after sulfuring and liming, as shown in Table I, with those of the kieselguhr-carbon treatment of Table II.

KIESELGUHR-CARBON PROCESS—The kieselguhr-carbon runs were made as follows: To each clarifier of raw mill juice (about 3000 lbs.) were added 20 lbs. (0.66 per cent) of kieselguhr. The juice was heated just to boiling and filter-pressed. On running clear, the juice was returned to the clarifier and to it were added 30 lbs. (1 per cent ash-and-moisture-free basis) of decolorizing carbon. This mixture was again brought to boiling and filter-pressed.

Samples of the mixed raw mill juice and the juice after each treatment were used for the analytical determinations. For dialysis, 200-cc. samples were treated as described in the sulfur-lime process.

The results of dialysis are given in Table II. The raw mill juice is designated by R, the kieselguhr-treated juice by K, and the carbon-treated juice by C. The first column of figures shows colloidal solids remaining after each treatment, expressed in mg. per 100 cc. The second column gives the per cent colloids calculated on the amounts before and after treatment. The last column gives ash in mg. per 100 cc.

It will be noted by comparison with Table I that, in general, less colloids are found in the juice after kieselguhr treatment alone than after sulfuring and liming. It may be supposed that liming contributes to the total colloids in the latter process, the supposition being well borne out by comparing the figures for ash. It is also known that the colloids of cane juice are reversible to acids and alkalies.

Table II—Kieselguhr-Carbon Clarification -Colloids by Dialysis

Run	Carbon Used	Kind of Juice	Total Colloids Mg. per 100 Cc.	Colloids Per cent Left	Ash Mg. per 100 Cc.
4	A	R	152.8	.....	13 8
		K	22.6	14.79	3.3
		C	11.1	49.11	3.0
5	B	R	129.9	.....	18 5
		K	31.8	24.50	3.2
		C	11.4	35.85	3.7
6	C	R	225.9	.....	12.2
		K	37.1	16.42	5.1
		C	11.3	30.45	1.9
7	D	R	182.1	.....	14 7
		K	33.3	18.28	4.9
		C	23.4	70.27	3.9
8	A	R	407.1	.....	40 4
		K	45.8	11.25	7.9
		C	18.8	41.05	3.6
9	B	R	327.2	.....	56.1
		K	42.6	13.02	5.2
		C	31.9	74.64	3.4
10	D	R	243.9	.....	27.6
		K	34.7	14.23	4.5
		C	34.4	99.13	4.5

In Runs 4, 5, 6, and 7 of Table II the raw juice samples were centrifuged before dialysis in order to remove mud and some of the suspended matter. In Runs 8, 9, and 10 the raw juice samples were not centrifuged. A comparison of these two sets of figures furnishes an idea of the kind and amount of material removed by treatment with kieselguhr alone. There is a variation in the amounts of colloids left after kieselguhr treatment which is no doubt due to variations in the tightness of the rolls in grinding. Such variation may perhaps also be explained by changes in the condition of the cane, part of which had been exposed to several frosts.

COLORIMETRIC DETERMINATIONS—Table III contains the results of colorimetric determinations. These were made with the Hess-Ives tint-photometer in the manner described by Meade and Harris,[1] the table worked out by them being used for translating scale readings of the instrument to units of color. The different carbons are designated by the letters A, B, C, and D, and the juice after treatment with kieselguhr and carbon by K and C, respectively. The first three columns of figures were obtained by subtracting from 100 the scale readings of our instrument, which, it happens, reads in a reverse direction from that used by Meade and Harris. The second three columns of figures are translations to color units. The seventh column contains the total color units divided by 3, and the last column shows the percentage of this total left in the juice after carbon treatment.

Two runs were made with each carbon, but through a mishap at the sugar house the second run with Carbon C was lost.

A variation in decolorization is particularly noticeable in Runs 4 and 8 in which Carbon A was used, and in Runs 5 and 9 where Carbon B was employed. In attempting to explain this we would point out that in the second runs with each of these carbons a greater amount of total colloids was present in the juice after kieselguhr treatment in each case, which no doubt interfered with adsorption of coloring matter.

---

[1] This Journal, **12** (1920), 686.

TABLE III—KIESELGUHR CARBON CLARIFICATION—DECOLORIZATION

Run	Carbon Used	Kind of Juice	Scale Readings Red Screen	Scale Readings Green Screen	Scale Readings Blue Screen	Color Units, Meade's Table Red Screen	Color Units, Meade's Table Green Screen	Color Units, Meade's Table Blue Screen	$\frac{\text{Total Units}}{3}$	Per Cent Color Remaining
4	A	K	28	15	9	126.6	189.0	239.5	185.3	....
		C	93	83	100	7.2	18.6	0.0	8.6	4.64
5	B	K	24	14	9	141.9	196.0	239.5	192.5	....
		C	96	85	81	4.0	16.2	21.0	13.7	7.12
6	C	K	25	12	7	137.8	211.0	264.0	204.2	....
		C	100	100	68	0.0	0.0	38.4	12.8	6.28
7	D	K	32	16	10	113.3	182.0	229.0	174.8	....
		C	100	80	73	0.0	22.2	31.2	17.8	10.23
8	A	K	25	14	8	137.8	196.0	251.0	194.9	....
		C	92	88	58	8.3	12.7	54.2	25.0	12.82
9	B	K	40	29	19	91.1	123.1	165.0	126.4	....
		C	90	81	70	10.5	21.0	35.5	22.3	17.63
10	D	K	37	22	11	98.9	150.6	219.0	156.2	....
		C	85	81	72	16.2	21.0	32.6	23.3	14.92

It is probable that as the amount of total colloids increases, the decolorizing power of any carbon is diminished.

The molasses from the carbon runs contained material in suspension which settled out upon standing. A similar precipitate had been observed previously by Coates and Slater[1] in sirup from sulfur-lime treatment. We made a partial analysis of our precipitate from molasses after freeing it from soluble matter and found it to contain 75.93 per cent ash. The ash contained 52.22 per cent silicon dioxide, 15.61 per cent ferric oxide and alumina, and 10.23 per cent calcium oxide. Qualitative examination showed the presence also of phosphoric acid, magnesium oxide, and a considerable amount of copper. These findings are in qualitative agreement with those of Coates and Slater. We also obtained a strong reaction for manganese.

The proportion of carbon used in the above experiments, 1 per cent on the weight of juice, is perhaps the lowest that it is profitable to use in most cases.

REPEATED USE OF CARBON

In first reducing the juice to sirup as practiced at most of the sugar houses, or in refining raws, the proportion of carbon used is about 5 per cent based on total solids, which is nearly the same as our 1 per cent on juice. In order to gain a knowledge of what might be expected from repeated use of any particular carbon we made the following simple laboratory experiments, since the limited amount of cane available would not permit such tests to be run at the sugar house. Two hundred cc. of juice, first clarified with kieselguhr, were treated with 2 g. of decolorizing carbon, heated to boiling, and filtered by suction. When sucked dry the carbon was transferred to a second 200 cc. of juice, and the heating and filtration were repeated. The second filtration was in each case very much slower than the first, and on a third treatment, filtration was very difficult in most cases. Color determinations were made on each filtrate and the color units found by the use of the table of Meade and Harris.

The results of these experiments are shown in Table IV. Very good decolorization was obtained by a second filtration with Carbon A, while with Carbons B, C, and D little or no decolorization was obtained. By a third filtration, not only was filtration very slow, but coloring matter was actually washed out of Carbons B and D. It was practically impossible to filter Carbon C on third treatment. It would seem to be unprofitable to use less of the three latter carbons for cane juice decolorization than in the above proportions, while with Carbon A fair results might be expected with half this quantity.

TABLE IV—REPEATED FILTRATION WITH SAME CARBON COLOR REMAINING AFTER FILTRATION

Juice before Carbon Treatment

	Instrument Readings	Color Units	$\frac{\text{Total Units}}{3}$
Red screen	50	68.9	
Green screen	34	107.3	
Blue screen	20	160.0	112.0

	First Filtration Inst. Readings	First Filtration Color Units	Second Filtration Inst. Readings	Second Filtration Color Units	Third Filtration Inst. Readings	Third Filtration Color Units
Carbon A						
Red screen	69	37.0	57	55.9	45	79.4
Green screen	59	52.5	47	75.1	32	113.3
Blue screen	52	65.0	35	104.4	22	150.6
$\frac{\text{Total units}}{3}$		51.5		78.5		114.4
Carbon B						
	59	52.5	49	70.9	45	79.4
	48	73.0	36	101.6	32	113.3
	39	93.6	24	141.9	20	160.0
$\frac{\text{Total units}}{3}$		73.0		104.8		117.5
Carbon C						
	60	50.8	47	75.1		
	50	68.9	35	104.4		
	42	86.2	22	150.6		
$\frac{\text{Total units}}{3}$		68.6		110.0		
Carbon D						
	56	57.5	40	91.1	35	104.4
	50	68.9	33	110.3	25	137.8
	41	88.7	23	146.2	16	182.0
$\frac{\text{Total units}}{3}$		71.1		115.9		141.4

SUMMARY

1—Sugar-house and laboratory tests were made on four decolorizing carbons.

2—Tables are given which show the amounts of solids and ash left after sulfur-lime and kieselguhr-carbon treatments. In general, fewer colloids were found after the use of kieselguhr alone than after the sulfur-lime treatment.

3—Colorimetric determinations were made on the juice treated with the four different carbons.

4—Tests were also made of repeated use of the carbons. In the case of one carbon only, was good decolorization obtained on a second filtration.

The United States Civil Service Commission has announced an examination for the positions of bacteriologists at $130 to $180 a month, associate bacteriologist at $90 to $130 a month, assistant bacteriologist at $70 to $90 a month, and junior bacteriologist at $70 a month to fill vacancies in the Public Health Service throughout the United States. In addition to the salaries, appointees will be allowed quarters, subsistence, and laundry, and may be allowed the increase granted by Congress of $20 a month. The duties of bacteriologists will require ability to identify the ordinary pathogenic microörganisms; to make and preferably interpret sections of pathologic tissues; to make examinations and analyses of water, milk, urine, stomach contents, and body fluids; to make blood counts and complement fixation tests. Associate bacteriologists must have familiarity with most of the preceding technic and capacity to learn any of it. Assistant bacteriologists must have familiarity with staining, culture making, bacteriologic diagnosis of infectious diseases, urinalysis, alkalies, and capacity for development. Junior bacteriologists must have qualifications similar to those of assistant bacteriologists. Competitors will be rated on education and training (30 points) and experience (70 points). Applications will be rated as received until December 1, 1921. Applicants should submit as part of their applications answers to the following questions:

1—Experience in clinical pathology, including urine analysis, examination of gastric contents, feces, sputum, blood, and puncture fluids.

2—Experience in clinical bacteriology, including preparation of culture media, staining, identification of microörganisms, and preparation of vaccines.

3—Experience in blood chemistry, including preparation of blood chemical reagents and quantitative estimation of blood urea nitrogen, uric acid, creatinine, sugar, cholesterol, carbon dioxide, and other blood chemical constituents.

4—Experience in serology, including the Moss grouping of cells prior to transfusion, Widal and similar agglutination tests, and the complement fixation test for syphilis.

5—Experience in histopathological technic including preparation of stains, sections and the gross preparation of tissues for museum purposes.

Ability to do a satisfactory Wassermann reaction is absolutely necessary.

---

[1] THIS JOURNAL, 8 (1916), 789.

Dry Substance in Molasses, Sirups and Juices by the Spencer Electric Oven[1]

By George P. Meade

Central Control Laboratory, Cuban-American Sugar Co., Cardenas, Cuba

The design of the Spencer electric oven and its use for drying granular and fibrous substances, such as raw sugar, press-cake, bagasse, cotton, etc., have been described by Dr. G. L. Spencer.[2] Essentially, the oven is a device by means of which a large volume of heated air is drawn through the substance to be dried. The heating element is a coil of resistance wire connected in series with a sliding rheostat so that the temperature of the air may be controlled. The air is drawn over the heated coil, and through a capsule containing the sample, by a vacuum pump or steam ejector. The oven is made in two sizes, the smaller size being used in the experiments here described. The capsule is a metal cylinder, 3 cm. in diameter × 4 cm. high, fitted with a bottom of metal filter cloth to permit the air to pass freely.

To make the oven available for drying solutions, Dr. Spencer suggested that the liquid might be absorbed on asbestos, somewhat after the Babcock method of drying milk.[3] Accordingly, experiments were carried out based on the following method: The capsule is filled with freshly ignited, fluffy asbestos, loosely packed, and the whole weighed. The capsule holds about 6 g. of asbestos. The liquid to be dried is run on the asbestos, drop by drop, in an amount not to exceed 4 cc., and the capsule, plus sample, is again weighed. The air current of the oven is then turned on and the oven heated to 110° C., after which the capsule is placed in the oven, the temperature is again brought to 110°, and maintained at that point throughout the heating period, while the full current of air is drawn through the sample. At the end of the period the electric current and the air are both shut off, and the capsule is removed to a desiccator, cooled, and weighed.

All of the work here reported was done with one capsule only in the oven at a time, with the other holes well stoppered. This was found necessary for accurate work, as the laboratory air-pump did not give a sufficiently large volume of air for two capsules at once. Furthermore, with two capsules in the oven at a time, one sample frequently dried faster than the other, owing probably to the fact that the asbestos was less closely packed in one capsule than in the other.

TABLE I—DRY SUBSTANCE DETERMINED IN KNOWN SOLUTIONS OF REFINED SUGAR IN WATER

Per cent Sugar Taken	Weight of Sample Dried Grams	Per cent Solids Found		
		After 10 min.	After 15 min.	After 20 min.
23.71	6.2245	23.68	....	....
23.71	4.8285	23.71	....	....
24.35	3.1712	24.33	24.33	....
31.02	3.2310	31.20	31.15	31.11
35.02	2.7948	35.15	35.06	35.02
44.42	6.0437	44.71	44.57	44.57
44.42	5.9998	44.67	44.65	44.54

The results of tests on aqueous solutions of refined sugar are given in Table I. It is seen that in all cases with pure sugar solutions more than 99 per cent of the water is driven off in 10 min., and with the thinner solutions it is all driven off in that time. Practically constant weight is reached in all cases after 15 min.

TABLE II—SOLUTIONS OF RAW SUGAR IN WATER

(15 g. of raw sugar containing 1.02 per cent moisture dissolved in distilled water and made to 100 cc. weighed 105.346 g. = 14.09 per cent solids)

$$\left[\left(\frac{(98.98 \times 15.00)}{100}\right) \div 105.345\right]$$

Per cent Solids Taken	Weight of Sample Dried Grams	Per cent Solids Found	
		After 10 Min.	After 15 Min.
14.09	2.9370	14.15	14.13
14.09	3.4234	14.11	14.11

The solution described in Table II was made up to simulate to some extent a raw cane juice. The results are like those for the thinner pure sugar solutions.

In order to see the effect of the temperature of 110° on an easily decomposable substance such as levulose, various solutions of invert sugar and salt were made by inverting known weights of refined sugar with hydrochloric acid, and neutralizing the acid with standard sodium hydroxide. The percentage of combined solids was calculated from the weight of invert sugar plus the weight of salt formed by the acid and alkali, divided by the weight of the solution.

TABLE III—SOLUTIONS CONTAINING KNOWN WEIGHT OF INVERT SUGAR AND SODIUM CHLORIDE

Per cent Solids Taken (Invert Sugar + NaCl)	Weight of Sample Dried Grams	Per cent Solids Found		
		After 10 Min.	After 15 Min.	After 20 Min.
25.38	3.1720	25.60	25.46	25.39
25.38	3.2294	25.72	25.52	25.49
29.61	3.7995	29.95	29.72	29.63
29.61	3.6584	29.97	29.72	29.69
33.73	3.1855	33.90	33.77	33.74
33.73	3.3592	33.79	33.71	33.69

Invert sugar and salt solutions (Table III) give much the same class of results as are obtained with pure sugar solutions. Only a fraction of a per cent of water remains after 10 min.' heating. The agreement, after 20 min.' heating, between the known solids and the solids found, is invariably very close, indicating that no destruction of levulose takes place in that length of time. No discoloration was apparent in any of the samples.

TABLE IV RAW CANE JUICE

Sample No.	Weight of Sample Dried Grams	Per cent Solids Found		
		After 10 Min.	After 15 Min.	After 20 Min.
1	3.2747	15.78	15.76	15.76
1	3.5554	15.75	15.75	....
2	3.7282	20.29	20.28	20.28
2	3.2931	20.33	20.32	20.32

The results of tests with raw cane juice are given in Table IV. It is evident from these tests that 10 min. is sufficient to dry juices, and such thin solutions as are of low viscosity. The agreement between duplicates in many other juice tests not listed has been found to be practically as good as those reported above.

TABLE V RAW SUGAR FACTORY FINAL MOLASSES

(Dilution 1:1 except where noted)

Sample	Weight of Dilute Solution Dried	Per cent Solids (Dil. Sol.)			Per cent Water in Orig. Molasses (Calc. from 20-Min. Period)	REMARKS
		10 Min.	15 Min.	20 Min.		
	3.5390	39.98	39.68	39.59	20.82	
	3.6126	39.93	39.68	39.52	20.96	
	3.0910	39.90	39.81	39.67	20.66	
	4.1123	19.94	19.89	19.82	20.72	Dilution 1:3
	4.1115	....	....	39.59	20.82	Tests made in factory lab.
	4.0854	....	....	39.60	20.80	
M5	3.4766	40.23	40.06	39.93	20.14	No change in wt. on heating 5 min. more
	3.5566	40.22	40.05	39.91	20.18	
	3.0920	40.65	....	39.88	20.24	Tests made in lab. of factory of origin
	3.0300	40.50	....	39.83	20.34	
D5	3.2058	40.14	....	39.80	20.48	Extra heating periods showed continued loss, not checking in the various duplicates
	3.4467	40.38	....	39.71	20.58	
	2.4570	....	....	39.66	20.68	
	3.3774	....	....	39.72	20.56	
D4	2.7900	....	....	40.26	19.48	Duplicates failed to check after 30 min. heating
	3.3932	40.64	40.38	40.20	19.60	
	3.2876	40.50	40.24	40.11	19.78	
	4.1094	20.32	20.16	20.06	19.76	Dilution 1:3

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] THIS JOURNAL, **13** (1921), 70.

[3] U. S. Department of Agriculture, *Bulletin* **46** (Revised Ed., 1899), 54.

Materials high in solids, such as molasses, sirups, and honey, must be diluted with an equal weight of water so that the asbestos will absorb the liquid. In the case of molasses, this dilution offers no added manipulation in raw sugar factory practice, since the "double dilution" method is routine procedure for molasses densities by the Brix hydrometer. A portion of this solution may be conveniently used for the moisture determination in the Spencer oven. In the runs recorded in Table V, dilution of 1 : 3 was tried in two cases, as noted, to see whether the more dilute solution would dry more rapidly.

The work with molasses shows the same general trend as the results with known solutions, in that nearly all of the water is driven off in the first 10 min. The moisture in the original molasses, calculated from the solids obtained after 20 min.' drying, shows good agreement between duplicates, considering that the variations are multiplied on account of the dilution employed. Nothing is gained by using a 1 : 3 dilution. In those cases where samples were subjected to extra heating beyond 20 min., the results were erratic.

Based on the work with known solutions, together with the work on the molasses, the conclusion seems safe that 20 min.' heating with the air at 110° C. is the correct period to employ for this class of material. Heating to constant weight should not be attempted.

TABLE VI STRAINED HONEY
(Diluted 1:1 by weight)

Weight Dilute Solution Dried	Per cent Solids (Dil. Sol.) 10 Min.	15 Min.	20 Min.	Per cent Moisture Original (Calc. from 20-Min. Period)
3.6362	37.03	36.90	36.89	26.22
4.8078	37.02	36.89	36.88	26.24
4.0930	37.14	37.01	36.99	26.02

In three tests on honey recorded in Table VI constant weight was reached in 15 min. The original honey was thin, probably diluted by the seller, which accounts for the relatively high percentage of moisture.

SUMMARY

By absorbing the liquid on asbestos, after the manner of the Babcock method of drying milk, the Spencer electric oven may be used for determining dry substance in solutions.

Known solutions of sugar, and of invert sugar and salt, are dried to practically constant weight in 20 min., the agreement between solids taken and solids found being to 1 part in 300, or better.

Thin solutions of low viscosity, such as cane juice, are fully dried in 10 min.

Molasses, sirups, and honey must be diluted 1 : 1 by weight with water before drying. The heating period for these materials should be 20 min. at 110° C., and no attempt should be made to reach constant weight by extra heating periods.

For work of this character a very strong current of air through the oven is required.

The Determination of Reducing Sugars in Lead-Preserved Cane Juices[1]

By **Joseph B. Harris**

CENTRAL CONTROL LABORATORY, CUBAN-AMERICAN SUGAR CO., CARDENAS, CUBA

The percentage of glucose or reducing sugars in cane-sugar factory products is used for the calculation of "glucose ratios" and "glucose balances" for the purpose of knowing whether sucrose is being inverted, or glucose being destroyed, at any stage of the process. For this purpose the best comparative figure is that obtained by making the determination on the material without the use of lead, thus showing all copper reducing substances, and leaving no question as to an indeterminate amount of reducing substance precipitated or changed by the lead. Since the figure is used only for the comparison of relative amounts of reducing substance in the various stages of the process, the question as to the presence of reducing substances, not reducing sugars, is of no interest. In this paper the term "reducing sugars" or "glucose" is used to mean all copper-reducing substances present in the material.

The determination of the reducing sugars without the use of lead on the heavier materials, such as sirup, molasses, or sugars, is very simple, since the composite samples can be kept for a reasonable length of time, but for compositing juice samples a preservative is necessary. Dry basic lead acetate, in the proportion of 20 g. per liter of juice, has been found the most effective preservative, so that for comparative purposes the problem of determining the reducing sugars in the juice becomes that of seeking a reagent for deleading that will overcome the effect of the lead and give the same result as would have been obtained had the juice been analyzed without the use of lead.

The present investigation was taken up for the purpose of finding such an agent for the lead-preserved juice, which would give results comparable to those of the sirups, molasses, and sugars on which the reducing sugars have been determined without lead for several years.[1]

EXPERIMENTAL PART

A number of samples of raw cane juice were divided in two portions, the amount of copper reduced being determined on one untreated portion, after filtering without lead, using kieselguhr only to aid filtration. For the purposes of the investigation this gives the true amount of reducing sugars. At the same time 20 g. of dry basic lead acetate per liter were added to the other portion, which was shaken thoroughly and left standing for 24 hrs. The leaded portion was then reshaken, and 100-cc. portions of the leaded juice, roughly measured in a graduated cylinder, were treated with the following reagents:

0.75 g. dry sodium oxalate
1.0 g. sodium chloride
1.5 g. sodium bicarbonate
0.5 g. pulverized crystals of oxalic acid
0.2 to 0.3 cc. phosphoric acid—85 per cent, C. P.
0.2 to 0.3 cc. acetic acid—99.5 per cent, C. P.
No deleading agent

After treatment with the reagents the juice was filtered, and the amount of copper reduced was determined on the filtrate.

Copper reduction was carried out by the Meissl and Hiller method: 50 cc. of the solution for analysis (containing 10 to 15 g. of juice) and 50 cc. of mixed Fehling solution were heated to the boiling point in a beaker on an electric hot plate in 4 min., and maintained at gentle ebullition for exactly 2 min. The boiling point was determined by a thermometer in the liquid. At the end of the boiling period, 100 cc. of cold, recently boiled, distilled water were added, the solution filtered through an alundum crucible. The cuprous oxide was burned to cupric oxide and weighed as cupric oxide. The results are given in the following tables:

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921

[1] Meade and Harris, THIS JOURNAL, 8 (1916), 504.

Table I—Tests without Lead Compared with Tests after Deleading with Sodium Oxalate, and Tests without Deleading

Without Lead	Deleaded with Sodium Oxalate	Filtered without Deleading
CuO	CuO	CuO
0.3598	0.3440	0.3505
0.2869	0.2746	0.2797
0.3585	0.3533	0.3514
0.3083	0.2896	0.2914
0.3003	0.2892	0.2913
0.3144	0.3048	0.3048
0.2351	0.2251	0.2246
0.2345	0.2266	0.2243
0.0743	0.0659	0.0659
0.0743	0.0645	0.0661
0.2546	0.2438	0.2450

With 10 g. of juice used per test, and assuming a polarization of 12.00, the percentage of glucose without lead is 1.04 and after deleading with sodium oxalate, 0.99, a difference of 5 per cent on the total.

Taking the figure without lead as correct, deleading with sodium oxalate gives too low results, and comparison with tests made on the filtrate from leaded juice without any deleading agent shows nothing accomplished by deleading with sodium oxalate. The filtrate after deleading with sodium oxalate is decidedly alkaline to phenolphthalein and to litmus.

Table II—Comparison of Tests without Lead and after Deleading with Sodium Chloride

Without Lead	Deleaded with Sodium Chloride
CuO	CuO
0.3598	0.3498
0.3083	0.2926
0.3003	0.2815

The reducing sugars combined with the lead cannot be recovered by treating with sodium chloride, the error being greater than with sodium oxalate.

No further tests with normal salts were made, it being assumed that in order to recover the combined reducing sugars the basicity of the lead would have to be neutralized with acid salts or acids.

To try the effect of acid salts, sodium bicarbonate was used as a deleading agent.

In the majority of tests the sodium bicarbonate checks the tests without lead very closely and the average is well within the limits of accuracy of the test, but a number of very erratic results, both lower and higher than without reagents, show that it is not dependable and is not to be recommended as a deleading agent.

Table III—Comparison of Tests without Lead with Tests after Deleading with Sodium Bicarbonate

Without Lead	Deleaded with Sodium Bicarbonate	Difference
CuO	CuO	CuO
0.3135	0.3218	+0.0083
0.2427	0.2407	—0.0020
0.3588	0.3554	—0.0034
0.3161	0.3170	+0.0009
0.0733	0.0735	+0.0002
0.1477	0.1460	—0.0017
0.2421	0.2401	—0.0020
0.1954	0.1912	—0.0042
0.1944	0.1911	—0.0033
0.2869	0.2804	—0.0065
0.3585	0.3571	—0.0014
0.3376	0.3354	—0.0022
0.3058	0.3023	—0.0035
0.2645	0.2769	+0.0124
0.3003	0.3013	+0.0010
0.3144	0.3140	—0.0004
0.3233	0.3248	+0.0015
0.2871	0.2835	—0.0036

In every case the tests after deleading with oxalic acid agree very closely with the tests without lead. Several of the tests were made with anhydrous oxalic acid, but since it is very hygroscopic it is doubtful if any greater accuracy is obtained by its use. At any rate, the dilution due to the water of crystallization of the oxalic acid is shown to be within the limits of accuracy of the test and can be ignored. There is no indication of inversion by the oxalic acid. Since it reacts with the lead acetate to form lead oxalate, the acidity of the filtrate is probably due entirely to acetic acid formed in the reaction, and the high inverting power of the oxalic acid offers no danger.

Table IV—Comparison of Tests without Lead with Those after Treating with Acids

Without Lead	Deleaded with Oxalic Acid	Deleaded with Phosphoric Acid	Treated with Acetic Acid
CuO	CuO	CuO	CuO
0.3376	0.3371	0.3379	0.3301
0.3233	0.3255	0.3262	0.3165
0.3366	0.3354	0.3314	0.3288
0.3382	0.3368	0.3325	0.3294
0.2869	0.2869	0.2879	......
0.3585	0.3576	0.3610	......
0.3058	0.3051	0.3039	......
0.3003	0.3010	0.2998	......
0.3144	0.3127	0.3164	......
0.3233	0.3255	0.3262	......
0.2871	0.2860	0.2838	......
0.2645	0.2650	0.2695	......
0.3135	0.3130	0.3080	......
0.3025	0.2997	......	......
0.2427	0.2420	......	......
0.3588	0.3575	......	......
0.3161	0.3168	......	......
0.1477	0.1462	......	......
0.2421	0.2415	......	......
0.1959	0.1944	......	......
0.1800	0.1819	......	......
0.0733	0.0747	......	......

The phosphoric acid checks the tests without lead very well in some cases, but a number of variations of 4 to 5 mg. of CuO, both higher and lower than the tests without lead, show it to be less dependable than oxalic acid.

Acidifying with acetic acid before filtering gives low results. The amount added was not sufficient to account for the low results by dilution. It is possible that sufficient acetic acid might be added to release the reducing sugars combined with the lead, but this would introduce a considerable dilution error, very difficult to measure on account of the difficulty of measuring the leaded juice accurately.

The dilution error in the case of the other reagents is partly compensated for by the formation of a precipitate with the lead, and is shown by the tests to be within the limits of accuracy of the determination.

Since oxalic acid had given the best results, the following tests were made, deleading with oxalic acid after filtering off the lead precipitate. The oxalic acid was added to the filtrate in the same proportion as in the other tests, *i. e.*, 0.5 g. per 100 cc. of filtrate.

Table V—Comparison of Tests without Lead and Tests on the Filtrate not Deleaded and Deleaded with Oxalic Acid

Without Lead	Filtrate not Deleaded	Filtrate Deleaded with Oxalic Acid
CuO	CuO	CuO
0.2433	0.2257	0.2261
0.1849	0.1771	0.1767

These tests show that the addition of deleading agents after filtering off the lead precipitate is useless. To be effective, the deleading agent must be added to the leaded sample before filtering.

Summary

The percentage of reducing sugars as obtained on juice samples preserved with basic lead acetate after deleading with the usual normal salts is too low.

To obtain the full percentage of reducing sugars in lead-preserved samples of juices it is necessary to use an acid deleading agent before filtering.

The use of deleading agents after filtration has no effect.

Oxalic acid is shown to be the most effective reagent tried for the purpose, always giving results which check tests on the same juice before preserving with lead.

The Link-Belt Company of Chicago has acquired all of the capital stock of the H. W. Caldwell & Son Co., and Frank C. Caldwell has been elected a director of the Link-Belt Company. The Caldwell plant will continue to be operated under separate corporate existence and under its present name, the plant management remaining substantially unchanged.

The Preservation of Fish Frozen in Chilled Brine. I—The Penetration of Salt[1]

By **L. H. Almy** and **E. Field**

Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.

The advantage derived from storing fish in the hard frozen condition in order to preserve them during the period when production exceeds consumption is well recognized throughout the greater part of the country. Judging from the results obtained, the methods now employed for the freezing and storing of fish[1*] appear to be quite satisfactory. At the present time efforts are being made to introduce new processes for freezing fish. These processes involve the use of chilled salt brine in freezing the product, the latter being in direct contact with the solution for periods varying from 15 min. to 3 or 4 hrs. until hard frozen.

The detailed procedures recommended by the authors of these new methods differ in some respects. The fish may be immersed in the cold brine after they have been chilled to near 32° F.[2] or without having been thus precooled,[3] or they may be frozen in open shipping cases by passing chilled brine through the goods.[4]

Practical experiments performed by European investigators both on a laboratory scale[5] and under commercial conditions[6] indicate that the freezing of fish in brine has many points in its favor. It does not take as long to freeze in brine as it does in air. During the slow freezing by the latter method fish lose in weight somewhat, as the result of a slight evaporation of water. This, of course, does not take place in fish while being frozen in brine. It has been thought by some that the method would be cumbersome to operate. It is possible, however, by the use of suitable mechanical devices[7] to make the process continuous and to freeze fish with very little labor. It seems to be well adapted for use on fishing boats[8] and to be practical for the commercial freezing of fish on land.[9]

Droogleever Fortuyn,[10] who examined histologically the flesh of fish frozen in air and in brine, states that the muscle fibers of fish frozen according to the latter method "swelled up and returned to their original form better than in other cases, when thawed." According to Reuter,[11] during the freezing in brine the fluids in the muscle fibers near the outer surface of fish congeal practically *in situ,* while the fluids in the muscle fibers deep in the body of a large fish exhibit a tendency to withdraw toward the center of the fibers, eventually forming single columns of ice crystals. Also, in the case of fish frozen slowly, as in the present air process, the separation of fluids is much more marked, the water escaping from the ruptured sheaths of the fibers and accumulating in the form of large ice crystals between compressed masses of fibers. It would seem that, since less change occurs in the muscular tissue of fish frozen in brine than in that of fish frozen in air, the former would more nearly resemble fresh unfrozen fish in texture and flavor than would the latter.

There thus appear to be advantages to be derived from the use of chilled brine for freezing fish. It is not the object of this paper, however, to discuss in detail the relative merits of these two general processes. A just comparison must necessarily await such time as the trade has given the new method a thorough trial, as little is now known by the trade of this country concerning the ease and economy of its operation under commercial conditions.

For the successful preservation of fish in freezer storage it is necessary to limit the evaporation of water from the fish to a minimum. This is accomplished efficiently and economically by means of an ice glaze. Such a glaze, by retarding the drying out of the fish, tends to preserve not only the quality of the flesh but also the external appearance. In deciding concerning the usefulness of the brine method for preparing fish for freezer storage, it is important for one to know whether fish which have been frozen by that method will retain a glaze for a reasonable period of time. The Food Investigation Board of Great Britain,[12] which touched upon this question in connection with its general study of the brine freezing of fish, found that salt was retained by the surface of the fish, the amount being directly proportional to the concentration of the brine and very nearly proportional to its temperature. The conclusion was reached "that, if glazing be insisted upon as necessary for prolonged preservation, brine freezing is at a disadvantage." Plank, Ehrenbaum, and Reuter[13] report some experiments which indicate that the penetration of salt into the tissues of fish is not as great when the temperature corresponds to a point on the ice curve of the freezing solution as when the temperature is higher. The amount of salt absorbed when fish were frozen in unsaturated brine solutions at or slightly below their freezing points was found to be comparatively small.

In view of the prominent part which the process of glazing plays in the successful preservation of fish in freezer storage in this country, a study was made of the degree of salt penetration into the skin and superficial tissues of weakfish (*Cynoscion regalis*), flounders (*Pseudopleuronectes americanus*), herring (*Clupea harengus*), and whiting (*Merluccius bilinearis*), during immersion for different periods of time in cold brines of different temperatures and concentrations.

METHODS

FREEZING APPARATUS—A wooden tank 46 in. long × 23 in. wide × 36 in. deep, lined with galvanized iron was fitted with brine coils lining the sides and ends. The flow of brine through the coils was regulated by means of inlet and outlet valves. The inlet pipe was connected to the calcium chloride brine line of a fish freezer at Manasquan, N. J., and the outlet pipe delivered the brine to a storage tank above, whence it reëntered the system to be recooled. The calcium chloride brine of the fish freezer at this time was being maintained at temperatures below —15° F. The salt brine in which the fish were frozen was made up of desired strength in the tank with the assistance of a hydrometer.

FREEZING OF FISH—Small quantities of fish were lowered into the cold brine and held beneath the surface by means of suitable weights. By constantly adjusting the valves and agitating the solution the freezing medium was kept at constant temperature. Some lots of fish were precooled in air to about 32° F. before freezing, while others were placed in the brine without previous chilling. All fish immediately after removal from the solution were dipped momentarily in cold fresh water to remove surface brine.

ANALYSES OF FISH. *Sampling*—The fish were sampled while hard frozen. A section approximating a cylindrical quadrant in shape was cut from the mid-dorsal region. The skin of this section, after careful separation from the muscular tissue, was scraped to remove scales, and was then cut into fine pieces, divided into two portions, and placed in tared weighing bottles. From the piece of muscular tissue remaining two successive slices of known thickness were cut on the side which had been next to the skin. The slices were chopped into small pieces and transferred to tared weighing bottles. The samples, therefore, consisted of the skin (without scales) and first and second muscular layers.

Solids—Total solids were determined in a number of the

---

[1] Received May 19, 1921.

[*] Numbers in text refer to References at end of paper.

samples by drying the material to constant weight in tared porcelain dishes in a vacuum oven at 55° to 60° F.

Ash—The organic matter in the sample, after drying, was driven off in an electric muffle at temperatures below 750° F. The dish and contents were then weighed.

Sodium Chloride—The ash residue in the porcelain dish was treated with about 30 cc. of hot water, and allowed to cool. The solution was titrated with 0.1 *N* silver nitrate, using potassium chromate as an indicator.

Fat—The percentage of fat was determined in representative samples of the entire flesh of some of the fish in the usual manner[14] by extracting the water-free solids from about 10 g. of flesh with anhydrous alcohol-free ether for 16 hrs.

RESULTS OF EXPERIMENTS

The conditions to which the fish were subjected in these experiments were intended to cover nearly every type which might be encountered in the commercial freezing of fish in chilled brine. Penetration of salt into the skin and outer muscular tissue of the fish occurred in every instance, although many of the experiments were designed with a view to preventing the entrance of salt. The amount of salt entering was not sufficient in any case to affect the flavor of the fish after cooking. The percentage of penetrated salt in the outer layer of muscular tissue one-eighth inch in thickness was found to be from 0.32 to 6.22 per cent (dry basis) in the case of all fish so examined, the average being 2.88 per cent.

The salt used throughout the investigation was of the grade which is known as Ground Alum salt. It contained approximately 98.80 per cent NaCl, 0.90 per cent $CaSO_4$, 0.06 per cent $CaCl_2$, and 0.003 per cent $MgCl_2$.[15]

EFFECT OF BRINE CONCENTRATION AND TEMPERATURE—As is well known, salts dissolved in water cause a lowering of the freezing point of the solvent. The point at which ice begins to separate out under favorable conditions is a definite function of the concentration of the solute. If the temperature of an aqueous solution be maintained at its freezing point while water is being added to it, theoretically ice crystals should form, since the diluted solution would then be under its freezing point.

It is this property of solutions of which use is made in one of the brine freezing processes.[16] The concentrations and temperatures of the brine solutions are so adjusted that the solutions remain constant at or slightly under their freezing points during the entire freezing process. It is claimed that under these conditions penetration of salt into the tissues of the products frozen is prevented, making possible a "strictly indifferent and purely physical conservation of food commodities."

TABLE I—EFFECT OF BRINE TEMPERATURE ON SALT PENETRATION

Expt. No.	Fish	Temperature of Fish upon Entering Brine	Concentration of Brine	Temperature of Brine	Length of Time in Brine	Thickness of Muscular Layers Examined	Penetrated Sodium Chloride (Moisture-Free Basis)		
							Skin	1st Muscular Layer	2nd Muscular Layer
		°F.	%	°F.	Hrs.	In	Per cent	Per cent	Per cent
6002	Weakfish	60–70	15	12	3	0.125	3.98	2.33	0.57
6008		60–70	15	17	3	0.125	6.06	2.43	0.49
6008		60–70	15	17	3	0.125	3.15	0.42	0.36
6004		60–70	20	6	2	0.125	1.34	0.57	0.52
6004		60–70	20	6	2	0.125	2.50	0.50	0.63
6010		60–70	20	12	2	0.125	1.87	0.67	0.60
6010		60–70	20	12	2	0.125	1.90	0.32	0.36
6012		60–70	25	0	1.5	0.125	14.12	2.51	0.59
6012		60–70	25	0	1.5	0.125	9.05	3.45	0.35
6014		60–70	25	6	1.5	0.125	7.26	3.90	0.86
6014		60–70	25	6	1.5	0.125	6.49	6.62	1.69
6015		60–70	25	12	1.5	0.125	9.50	4.71	1.85
6015		60–70	25	12	1.5	0.125	5.59	3.81	1.78
6030	Flounders	60–70	15	12	1	0.125	...	5.01	...
6031		60–70	15	17	1	0.125	...	4.84	
6013		60–70	25	0	1.5	0.125	6.99	2.37	0.28
6016		60–70	25	6	1.5	0.125	6.23	5.57	1.31
6017		60–70	25	12	1.5	0.125	9.79	1.56	0.59
6044	Whiting	31	15	17	1	0.09375	...	2.80	1.43
6047		31	15	12	1	0.09375	...	2.28	1.33

Weakfish, flounders, and whiting were frozen in sodium chloride solutions of different concentrations at their freezing points and at several degrees above these temperatures. In the former instances the presence of ice crystals in the freezing media was taken as an indication that the brine solutions were at the desired temperatures. The figures given in Table I indicate that salt penetration occurs under all conditions. The amounts of penetrated salt in the first and second muscular layers of fish frozen in 25 per cent brine at 6° F. and 12° F. were greater than they were in fish frozen in the same brine at 0° F. Also, in the case of the whiting frozen in 15 per cent brine, the higher temperature appeared to be more favorable for salt penetration. In the majority of cases, however, the degree of the penetration is not markedly influenced by the temperature factor.

In most of these experiments the temperature of the fish upon entering the brine was 60° F. to 70° F. Hence the difference in temperature between the fish and the various brines when at the lower temperatures was 48° F. to 70° F. The entrance into the cold brine of one or more such fish cannot fail to have some effect upon the temperature of the brine in immediate contact with the fish. This slight rise in temperature has the effect of retarding the process of freezing the outer surface of the fish. Therefore, appreciable salt enters the skin and the superficial muscular layer before the surface of the fish has congealed. It thus appears that, from the standpoint of the penetration of salt into fish, very little advantage is gained by endeavoring to keep the brine solution at the freezing point when the temperature of the product to be frozen is appreciably higher than that of the brine.

TABLE II—EFFECT OF CONCENTRATION OF BRINE ON SALT PENETRATION

Expt. No.	Fish	Temperature of Fish upon Entering Brine	Concentration of Brine	Temperature of Brine	Length of Time in Brine	Thickness of Muscular Layers Examined	Penetrated Sodium Chloride (Moisture-Free Basis)		
							Skin	1st Muscular Layer	2nd Muscular Layer
		°F.	%	°F.	Hrs.	In.	Per cent	Per cent	Per cent
6021	Weakfish	60–70	15	12	2	0.125	3.31	2.47	0.83
6010		60–70	20	12	2	0.125	1.87	0.67	0.60
6010		60–70	20	12	2	0.125	1.90	0.32	0.36
6025	Flounders	60–70	15	12	2	0.125	3.82	2.75	0.42
6011		60–70	20	12	2	0.125	4.15	3.28	0.81
6046	Whiting	31	18.9	12	1	0.09375	...	2.40	0.91
6047		31	15	12	1	0.09375	...	2.28	1.33

In the experiments reported in Table II an effort was made to determine the effect upon the degree of salt penetration produced solely by variations in the concentration of the brine. The amount of penetrated salt was slightly greater in the first muscular layer but less in the second in the case of whiting frozen in 18.9 per cent brine than it was in those frozen in 15 per cent brine, both being at 12° F. Flounders frozen in 20 per cent brine at 12° F. absorbed more salt in both muscular layers than did those frozen in 15 per cent at the same temperature. A corresponding increase in salt penetration with increase in brine concentration did not occur in the weakfish examined. A consistent relationship between salt penetration and brine concentration is not indicated by these experiments.

RATE OF SALT PENETRATION—Weakfish, flounders, herring, and whiting, as indicated in Table III, were immersed for 30, 60, 90 and 120 min. in 15 per cent brine at 12° F. Examination of the skin and outer muscular layers revealed the fact that in the case of weakfish and flounders the greater part of the salt penetration occurred during the first 30 min. of the freezing. In the herring and whiting the absorption of salt continued throughout the 2 hrs. in which the fish were under observation. The results indicate that the rate and amount of salt absorption varies with the species of fish, a subject which will be discussed in another section.

TABLE III—RATE OF SALT PENETRATION
(15 Per cent Brine at 12° F.)

Expt. No.	Fish	Temperature of Fish upon Entering Brine °F.	Length of Time in Brine Min.	Thickness of Muscular Layers Examined In.	Penetrated Sodium Chloride (Moisture-Free Basis) Skin Per cent	1st Muscular Layer Per cent	2nd Muscular Layer Per cent
6018	Weakfish	60–70	30	0.125	3.88	2.46	0.54
6018		60–70	60	0.125	3.38	2.27	0.57
6018		60–70	90	0.125	4.46	3.13	1.35
6018		60–70	120	0.125	3.31	2.47	0.83
6040		60–70	30	0.09375	4.72	2.32	0.92
6040		60–70	60	0.09375	6.53	2.49	1.09
6040		60–70	90	0.09375	6.52	3.25	1.18
6040		60–70	120	0.09375	7.88	1.70	0.75
6022	Flounders	60–70	30	0.125	4.40	4.11	0.59
6022		60–70	60	0.125	4.91	3.53	0.29
6022		60–70	90	0.125	6.40	3.82	0.66
6022		60–70	120	0.125	3.82	2.75	0.42
6041	Herring	60–70	30	0.09375	5.39	0.14	0.02
6041		60–70	60	0.09375	3.90	0.50	0.06
6041		60–70	90	0.09375	4.99	0.57	0.09
6041		60–70	120	0.09375	3.75	1.04	0.41
6042	Whiting	60–70	30	0.09375	4.06	2.28	1.13
6042		60–70	60	0.09375	4.31	3.05	1.45
6042		60–70	90	0.09375	5.36	4.39	1.98
6042		60–70	120	0.09375	5.79	5.44	2.45

The weakfish and flounders differed from the other two species of fish in another respect. There occurred a falling off in the per cent of salt in the first and second muscular layers after the former had remained for 90 min. in the brine. A plausible explanation of the phenomenon is that in the first few minutes during the immersion of the fish in the brine the rate of penetration of salt into the skin and outer muscular layer is faster than the speed of diffusion of this salt to the inner layers and that later the salt travels inward with greater speed than it is being replenished from without, the frozen exterior of the fish greatly retarding salt penetration. If the above expresses the true condition, then it must also be admitted that salt will tend to spread itself uniformly through the entire flesh of the fish, by diffusion inward, even after the tissues have become hard frozen. That this mode of action is probable is indicated by the fact that when a block of ice is immersed for 2 hrs. in chilled brine at its freezing point, salt will enter the ice and will proceed inward toward the center of the block after removal from the brine and while standing in air at the same temperature as the brine. The latter observation was made in connection with some experiments which were performed on the absorption of salt by ice, the results of which will be made the subject of a separate communication.

TABLE IV—EFFECT OF PRECOOLING ON SALT PENETRATION

Expt. No.	Fish	Temperature of Fish upon Entering Brine °F.	Temperature of Brine °F.	Concentration of Brine %	Length of Time in Brine Hr.	Thickness of Muscular Layers Examined In.	Penetrated Sodium Chloride (Moisture-Free Basis) 1st Muscular Layer Per cent
6028	Weakfish	60–70	12	15	1	0.125	4.98
6032		34	12	15	1	0.125	1.87
6036		34	12	15	1	0.125	1.31
6029		60–70	17	15	1	0.125	5.17
6033		34	17	15	1	0.125	2.69
6048	Whiting	56	12	15	1	0.09375	3.50
6047		31	12	15	1	0.09375	2.28

PRECOOLED FISH—Inasmuch as the penetration of salt is greatly retarded after the surface of the fish has become hard frozen, it is obvious that it might prove of advantage to precool fish before immersing them in the brine in order to hasten the freezing process and thus reduce the amount of salt absorption. The effect of such a procedure is illustrated by the figures in Table IV, showing the per cent of salt in the first muscular layer of weakfish and whiting, some of which were precooled to 31° or 34° F., and others of which were at temperatures between 50° and 70° F. just prior to immersion in the brine. There was considerably less absorption in the case of the precooled fish, the amount being 35 to 65 per cent of that occurring in those which were not precooled. In the practical operation of a plant, the chilling of the fish prior to freezing in this manner would necessitate a slight delay in completing the freezing process and would add somewhat to the cost of freezing the fish. In view of the fact that absorption of salt occurs in spite of this precaution, it would seem that such a procedure would hardly be justified from that point of view alone. These remarks apply only to freshly caught fish, as it is assumed that fish which have been out of the water for some time have been kept cold by one means or another and would, therefore, not require further precooling before treatment.

SALT PENETRATION AS A SPECIES CHARACTERISTIC—On examination of the figures in Tables I, II, III, and IV it will be noted that in several instances the amount of sodium chloride absorbed by the tissues varied in the same species even when all conditions, which could be controlled, were identical. These irregularities were due, it is believed, in part to differences in the composition of the outer muscular and cutaneous layers of the fish and in lesser degree to slight inequalities in the physical condition of the fish brought about in the handling prior to immersion in the brine. Although great care was exercised to prevent a bruising of the fish, it is possible that some of them may have received slight wounds which, though not visible to the naked eye, may have been effective in altering the resistance of the outer tissues to invasion by foreign material.

TABLE V—SALT PENETRATION AS A SPECIES CHARACTERISTIC

Expt. No.	Fish	Temperature of Fish upon Entering Brine °F.	Length of Time in Brine Hrs.	Thickness of Muscular Layers Examined In.	Penetrated Sodium Chloride (Moisture-Free Basis) Skin Per cent	1st Muscular Layer Per cent	2nd Muscular Layer Per cent
6019	Weakfish	60–70	1	0.125	3.38	2.27	0.57
6023	Flounder	60–70	1	0.125	4.91	3.53	0.29
6030	Flounder	60–70	1	0.125	....	5.01	....
6041	Herring	60–70	2	0.09375	3.75	1.04	0.41
6040	Weakfish	60–70	2	0.09375	7.88	1.70	0.75
6042	Whiting	60–70	[illegible]	0.09375	5.79	5.44	2.45

Aside from the individual variation in the same species, there appear to be marked species differences in the amount (Table V) and rate (Table III) of salt penetration. Arranging the fish in series, beginning with the species which absorbs the most salt and ending with the one which offers the most resistance to salt penetration, they assume the following order: whiting, flounder, weakfish, and herring. Mention has been made of the differences in the rate of salt penetration exhibited by weakfish and flounders on the one hand and whiting and herring on the other.

TABLE VI—DATA CONCERNING THE DISTRIBUTION OF FAT IN EXPERIMENTAL FISH ON DRY BASIS

Expt. No.	Fish	Weight of 1 Sq. In. of Skin (without scales) Gram	Fat-Free Weight of 1 Sq. In of Skin (without scales) Gram	Fat: Skin without Scales Per cent	Fat: Subcutaneous Tissue Per cent	Fat: Body Tissue Per cent
679	Whiting	0.0407	0.0391 (3)	3.86 (1)	4.74 (1)	0.52 (1)
676	Flounder	0.0743	0.0704 (4)	5.36 (2)	11.16 (2)	1.04 (2)
677	Weakfish	0.0769	0.0365 (2)	52.56 (4)	59.10 (3)	10.37 (3)
678	Herring	0.0627	0.0346 (1)	44.79 (3)	63.48 (4)	14.36 (4)

The analyses reported in Table VI were made in an effort to determine the causes responsible for these species differences. Comparisons were made of the dry fat-free weights of equal areas of scale-free skin and the per cent of fat in the skin, subcutaneous tissue and main body tissue of whiting, flounders, weakfish, and herring. If the numbers in each of the last four columns in this table are arranged in sequence of increasing values they will fall in the order indicated by the figures in parentheses opposite each number. It is seen that the order in which the fish fall on the basis of the fat content of the subcutaneous and body tissue is the same as that which they assume when arranged according to their increasing resistance to salt penetration.

It therefore appears that the presence of fat in these tissues tends to retard the entrance of salt. The latter substance in aqueous solution will penetrate fat-poor tissue with greater speed than it will the fat-rich tissue, partly because the amount of moisture in fatty flesh is less than it is in lean and partly on account of the mechanical retarding action of the solid fat in the chilled tissues. Variations in the proportions of subcutaneous fat would have a greater effect upon the extent of salt penetration than would differences in the per cent of body fat, as the proportion of water accompanying the former is much less than that associated with the latter and the adipose tissue is also more favorably situated to retard the entrance of the salt.

While the differences in the fat content of the superficial body tissues of the fish offer an explanation for the species variations in the amount of salt which penetrates in equal periods of time, they do not explain why herring and whiting differ markedly from weakfish and flounders in the *rate* of salt penetration. In the absence of evidence to the contrary it would seem that differences in skin and muscle structure might well account for the latter phenomenon.

Summary

Weakfish (*Cynoscion regalis*), flounders (*Pseudopleuronectes americanus*), herring (*Clupea harengus*), and whiting (*Merluccius bilinearis*) were frozen in chilled brine under different conditions to determine the various factors which influence the penetration of salt into the outer tissues of the fish. To assist in the determination of the degree of salt penetration, the skin and two successive layers of muscular tissue just beneath the skin were analyzed for their content of penetrated salt. The muscular layers examined were usually one-eighth of an inch in depth, a few being three-thirty-seconds of an inch thick. It was found that:

1—Salt penetrated perceptibly into the skin and superficial muscular tissues of all the fish under all conditions, the amount not being sufficient, however, to affect the taste of the cooked product.

2—During the process of freezing the above species of fish under various conditions, the outer muscular layer one-eighth inch in depth absorbed from 0.32 to 6.22 per cent of salt on the dry basis, the average being 2.88 per cent.

3—In a few instances the amount of salt absorbed by fish frozen in brine at its freezing point was slightly less than that which occurred when the brine temperature was several degrees above this point. In the majority of cases, however, no such temperature influence could be observed.

4—When fish were frozen in brines of different concentrations but at the same temperature, no consistent differences in the amount of salt absorbed by the fish could be noted.

5—Fish which had been precooled to near 32° F. before immersion in the brine did not take up as much salt as those which were at atmospheric temperature at this time, the absorption in the former case being 35 to 65 per cent of that in the latter.

6—The amount and rate of penetration of salt into the tissues of fish varies with the species. In weakfish and flounders the greater part of the salt which can be found in the superficial tissues at the end of a 2-hr. immersion in brine entered during the first 30 min. The absorption in the case of whiting and herring was more gradual, continuing rather uniformly during the two hours.

7—Inequalities in the fat content of the subcutaneous and body tissue of the fish are responsible in large measure for the differences in the susceptibility to salt penetration possessed by fish of the same species and by those of different species.

References

1—"The Commercial Freezing and Storing of Fish," U. S. Department of Agriculture, *Bulletin* **635**; E. D. Clark and L. H. Almy, "A Chemical Study of Frozen Fish in Storage for Short and Long Periods,' This Journal, **12** (1920), 656.

2—J. R. Henderson: U. S. Patent 1,055,636 (1913).

3—A. J. A. Ottesen: U. S. Patent 1,129,716 (1915); *Fish Trades Gazette*, October 20, **1917**, 39, 41, 43.

4—N. Dahl: U. S Patents 1,123,701 (1915), 1,177,308 (1916), 1,235,661 (1917), 1,367,024 (1921); H. J. Bull, U. S. Patent 1,201,552 (1916).

5—J. S. Gardiner and G. H. F. Nuttall: "Frozen Fish. Dry Freezing—Brine Freezing," *Fish Trades Gazette*, January 19, **1918**, 23, 25.

6—*Cold Storage and Produce Review*, **22** (1919), 173.

7—*Ibid.*, **23** (1920), 227.

8—*Ice and Refrigeration*, **49** (1915), 333.

9—The Frigus System, developed by N. Dahl, has been operated with profit at Throndhjem, Norway, for a number of years.

10—J. M. Bottemaine: "Notes on the Investigation of Preserving Fish by Artificial Cold." Preliminary Report, 3rd International Congress of Refrigeration, 3rd Section (The Netherlands), Washington-Chicago, **1913**, 27.

11—R. Plank, E. Ehrenbaum and K. Reuter: "Die Konservierung von Fischen durch das Gefrierverfahren," *Abhandlungen zur Volksernahrung*, issued by the Zentral-Einkaufsgesellschaft, **5** (1916), 218.

12—"Interim Report on Methods of Freezing Fish, with Special Reference to the Handling of Large Quantities in Gluts," Fish Preservation Committee, Food Investigation Board, Department of Scientific and Industrial Research, London, England (1920).

13—Plank, *et al.*, *Loc. cit*, 52–62.

14—Association of Official Agricultural Chemists, "Methods of Analysis," **1916**, 80.

15—Plans for determining the effect upon salt penetration produced by additions of calcium salts to the brine solution had to be abandoned when the chemical laboratory equipment at Philadelphia was dismantled on the occasion of the removal of the headquarters of the Food Research Laboratory to Indianapolis, Ind.

16—A. J. A. Ottesen: *Loc. cit.*

Labeling of Vinegar

The question as to the legal labeling of vinegar made from evaporated apples under the Federal Food and Drugs Act, which has been under controversy for some time, is to be litigated in the Federal Courts, according to a statement just issued by the Secretary of Agriculture. In February 1912, the Department of Agriculture in Food Inspection Decision 140 defined vinegar, cider vinegar, and apple vinegar as the product made from the alcoholic and subsequent acetous fermentations of the expressed juice of apples. This decision further provided that "the product made from dried apple skins, cores, and chops by the process of soaking with subsequent alcoholic and acetous fermentations of the solution thus obtained is not entitled to be called vinegar without further designation, but must be plainly marked to show the material from which it is produced."

Upon finding in the market vinegar made from evaporated apples but labeled as cider vinegar, the Department made a number of seizures. Some of the manufacturers elected to contest these cases in court, but the termination of such litigation has been delayed. In the effort to reach a satisfactory settlement of the question the Secretary of Agriculture, under date of July 14, 1921, called a public hearing and invited representatives of the industry, food law officials, and all interested parties to submit their views. The hearing was attended by a number of vinegar manufacturers, and letters were received from many state officials charged with the enforcement of food laws, and it was evident that the tentative suggestion of the Department that the term "apple vinegar" be permitted for vinegar made from evaporated apples is unsatisfactory to some of the manufacturers of such vinegar and to some of the manufacturers of vinegar from apple juice, as well as to many state food officials. The manufacturers of vinegar from evaporated apple stock claim that as their vinegar is made wholly from apples and apple products they have a right to use the descriptive terms "cider vinegar" and "apple cider vinegar," while the manufacturers of vinegar from fresh apple juice insist that Food Inspection Decision 140 be strictly adhered to. Pending the expected prompt decision of the court, no seizures will be made of vinegar made from evaporated apple stock and labeled "apple vinegar."

Measuring Soil Toxicity, Acidity, and Basicity[1,2]

By **R. H. Carr**

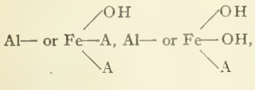
INDIANA AGRICULTURAL EXPERIMENT STATION, LAFAYETTE, INDIANA

It is well known that a very acid condition of the soil does not favor the best growth and development of many plants. The cause of this poor growth has been attributed to lack of calcium and magnesium plant food, to the presence of soluble salts of aluminium and iron which seem to be toxic to the plant, and to the presence of free acid (H-ion concentration) which is thought to be detrimental to the growth of many plants. The fact that aluminium salts are toxic has been reported by many workers.[3] The extent to which iron is toxic when associated with aluminium in acid soils is not so well understood, but it is believed by the writer that the conditions rendering it soluble enough to become toxic occur infrequently.

The writer has been making a study of soil composition and toxicity as related to the development of root rots of corn plants and has been trying to develop a method for determining soil acidity based upon the fact that, in the absence of calcium, magnesium, or other bases in the soil, the aluminium and iron salts can act as bases to form soluble salts. It was noticed by Comber[4] that when an alcoholic solution of potassium thiocyanate was shaken up with an acid soil a red color developed, somewhat in proportion to the acidity of the soil. This red color was due to the formation of ferric thiocyanate from soluble ferric iron in the acid soil. There was present in the alcoholic solutions also amounts of soluble aluminium which were in large excess over the amounts of iron in all of the soils that were tested. The presence of aluminium can be readily shown by the addition of a few drops of an alcoholic solution of logwood, where a blue color appears, somewhat in proportion to the amount of aluminium in the titrated solution of the acid soil. Iron compounds produce a brownish green color in the logwood solution.

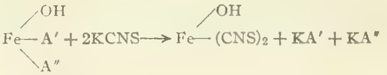
NATURE OF POTASSIUM THIOCYANATE ACTION

A study has been made of the nature of the action of potassium thiocyanate on the soil extract, and it is noted that the action is not simply one of double decomposition in the soil, as suggested by Comber, because other potassium salts extract very little or no iron from the same soils with which potassium thiocyanate gives a red color. Furthermore, an alcoholic solution of potassium ferrocyanide gives no indication of the presence of a soluble ferric salt with the same soil. The reaction is not simply between iron and aluminium already in solution and potassium thiocyanate, but the latter actually causes the solution of part of the iron and aluminium which may have existed previously as colloidal basic salts, *e. g.*,



$$\text{Al— or Fe}\begin{array}{l}\diagup\mathrm{OH}\\ \mathrm{—A}\\ \diagdown\mathrm{A}\end{array}\!,\ \text{Al— or Fe}\begin{array}{l}\diagup\mathrm{OH}\\ \mathrm{—OH}\\ \diagdown\mathrm{A}\end{array}\!,$$

releasing one, two, and three acid radicals, respectively (where A represents any acid radical). The reaction with the potassium thiocyanate may be written as follows:



$$\mathrm{Fe}\begin{array}{l}\diagup\mathrm{OH}\\ \mathrm{—A'}\\ \diagdown\mathrm{A''}\end{array} + 2\mathrm{KCNS} \longrightarrow \mathrm{Fe}\begin{array}{l}\diagup\mathrm{OH}\\ \mathrm{—(CNS)_2}\end{array} + \mathrm{KA'} + \mathrm{KA''}$$

When the ferric thiocyanate is titrated with a basic solution the reaction takes place as follows:

$$\mathrm{Fe(CNS)_3} + 3\mathrm{KOH} \longrightarrow 3\mathrm{KCNS} + \mathrm{Fe(OH)_3}$$

The red color of the $\mathrm{Fe(CNS)_3}$ acts as an indicator, the solution becoming colorless at pH 5.5. Ferric hydroxide does not give a red color with potassium thiocyanate solution when the pH is 5.4. It is possible that the release of the iron and aluminium is partly due to the increase in solubility upon adding an electrolyte not containing a common ion. This principle is made use of in a number of chemical determinations, as in the case of addition of ammonium chloride to free the alcohol solution from sodium sulfate ions in potassium determination.

If 2-g. samples of acid soil are shaken with any of the following salts: potassium chloride pH 5.3, potassium bromide pH 5.4, potassium iodide pH 5.8, potassium nitrate pH 5.2, sodium nitrate pH 5.7, calcium sulfate pH 5.5, and ammonium sulfate pH 5.4 in 95 per cent alcohol pH 5.3, making saturated solutions, and if a part of the solution is filtered and the filtrate tested for iron with potassium thiocyanate, there will be no evidence of iron present; if to the remaining unfiltered solution there be added a few cubic centimeters of potassium thiocyanate solution, a red color will appear, showing dissolved iron to be present. If the same soil is treated in the same way with potassium fluoride pH 8.2, potassium cyanide pH 7.7, calcium acetate pH 6.4, and calcium phosphate pH 6.5, there will be no indication of the presence of iron in either the filtrate or unfiltered part. In the former case the ionization of a salt of a strong acid with a strong base produces an acid solution ranging from pH 5.2 to 5.8, whereas in the latter case the solution is more basic (pH 6.4 to 8.2) and no red color appears in the soil mixture. Phosphoric acid ($\mathrm{H_3PO_4}$), on first addition to the soil, increases the red color, but continued addition of the acid causes the combination of all iron and aluminium as a phosphate, and the color disappears. The solutions of potassium thiocyanate and ammonium thiocyanate in 95 per cent alcohol are found to have an acidity of pH 5.3, and sodium thiocyanate an acidity of pH 6.5. Upon addition of potassium hydroxide solution the ferric thiocyanate solution produces potassium thiocyanate and becomes colorless at pH 5.5. It was found that the redness produced by the potassium thiocyanate and ammonium thiocyanate on an acid soil was of about the same degree, the potassium thiocyanate being slightly the more red, and both were much redder than sodium thiocyanate, which has a pH of 6.5. Soils which normally give a slight pink color with KCNS at pH 5.3 become redder if the acidity is increased to pH 5.0, and the color either does not develop at all or is much fainter than usual if the solution is made neutral to methyl red pH 6.0, or phenolphthalein pH 8.0, before being added to the soil.

Since the H-ion concentration of ammonium thiocyanate or potassium thiocyanate in alcohol had about the same pH, 5.3, the alcohol used being 5.4 (denatured alcohol had a pH of 6.2), it was expected that the lime requirements determined by the use of potassium thiocyanate and ammonium thiocyanate on the same soils would be about equal. It was found that the latter averaged about 6 per cent lower than the

---

[1] Presented before the Division of Agricultural and Food Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] The investigations on which this paper is based were conducted jointly by the Office of Cereal Investigations, U. S. Department of Agriculture, and the Indiana Agricultural Experiment Station.

[3] J. B. Abbott, S. D. Connor and H. R. Smalley, Indiana Agricultural Experiment Station, *Bulletin* **170** (1913); E. Kratzman, *Chem.-Ztg.*, **38** (1914), 1040; R. W. Ruprecht, Massachusetts Agricultural Experiment Station, *Bulletin* **161** (1915); K. Mikaye, *J. Biol. Chem.*, **25** (1916), 23; L. B. Hartwell and F. R. Pember, *Soil Sci.*, **6** (1918), 259; J. J. Mirasol, *Ibid.*, **10** (1920), 153.

[4] *J. Agr. Sci.*, **10** (1920), 420.

former, and sodium thiocyanate was over 50 per cent lower than either of the other salts. This is in accord with the amount of double decomposition taking place in a soil when salts containing potassium, sodium, or ammonium are shaken with a soil as noted by Kelley and Cummins.[1]

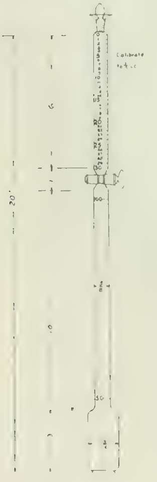
These data would seem to indicate that the action of potassium thiocyanate in an acid soil is one not only of double decomposition or metathesis, but partly solvent as well.

Since the iron content is quite variable in different soils it was surmised that there would not be sufficient iron available in some soils to give this indicator effect, especially in certain muck soils, but this was not found to be the case in many of the soils tested. The most acid muck the writer ever examined contained but 8 mg. of iron per 5-g. sample, and this soil gave a blood-red color to the potassium thiocyanate solution. It would be hard to find a soil containing a smaller amount of iron; however, in several acid muck soils examined no soluble iron was found in the potassium thiocyanate extract of the soil, yet on the addition of 3 drops of a 1 per cent ferric chloride solution a red color developed and titration could be made in the usual way. It is believed that acidity manifesting itself only upon addition of a ferric salt is of organic nature and much less harmful to growing plants. Several muck soils showing an acid reaction to litmus and no color with potassium thiocyanate solution did not respond to liming in the field. However, less extensive work has been done by the writer on the muck soil than on other types.

COLORIMETRIC METHOD UNCERTAIN

An attempt was made to work out a colorimetric method by using ten dilutions of the red solution from a very acid soil in order to get a rating on the limestone requirements of any soil, but the color was found to be quite fluctuating, and this method was not considered practical.

DETAILS OF METHOD



The following method was adopted to determine degree of acidity and amount of easily soluble iron and aluminium in soil. Place 50 g. of 10-mesh soil (25 g. of muck) in a 100-cc. glass-stoppered cylinder or in a specially designed glass tube, shown in the figure. Measure 30 cc. (50 cc. for muck) of a saturated solution (4 per cent) of potassium thiocyanate in 95 per cent alcohol (solution made to have a pH of 5.3) and pour on the soil. Stopper the cylinder and shake for 2 min. with an end-to-end movement. Place in an upright position and let settle for several minutes, and note the color of the supernatant liquid. If the liquid is pink or red, add from a buret a few tenths of a cubic centimeter at a time (depending on the color) a 0.10 *N* alcoholic solution of potassium hydroxide (made by adding a normal base to 95 per cent alcohol). Shake well after each addition and allow several minutes to settle. Continue the addition until the red or pink color has disappeared. Let stand over night and titrate out any pink which may develop. If too much base has been added, titrate back to a faint pink color with 0.10 *N* alcoholic acid. Note the number of cubic centimeters of 0.10 *N* base used. Each cubic centimeter of 0.10 *N* base required to neutralize the soil is equivalent to 200 lbs. of calcium carbonate per acre.

If no red color develops on addition of potassium thiocyanate, add from a buret a 0.10 *N* alcoholic solution of hydrochloric acid (made by adding normal hydrochloric acid to 95 per cent alcohol) until a pink color develops after standing several minutes. From the number of cubic centimeters of acid used the calcium carbonate equivalent of the soil may be determined.

LIME REQUIREMENTS AS INDICATED BY DIFFERENT METHODS

It is well known that the lime requirements of any soil as determined by the different methods vary greatly, so much so that nothing but the litmus paper test is even suggested in the latest revised methods of soil analysis. (A. O. A. C.) Table I gives some comparative figures on different methods.

TABLE I—LIME REQUIREMENTS BY DIFFERENT METHODS

SAMPLE NUMBER	POUNDS PER ACRE KCNS	Veitch $Ca(OH)_2$	Hopkins KNO_3	Jones $Ca(C_2H_3O_2)_2$
1	400	450	520	3490
2	1000	1000	50	2910
3	520	550	0	1380
4	1820	1850	500	2920
4*a* (Subsoil)	1750	1800	480	2190
5	700	700	150	1580
6	1020	1050	220	1500
6*a* (Subsoil)	1100	1100	75	1480
7	460	580	280	500
8	200	200	120	580
9	1000	1050	220	2200
9*a* (Subsoil)	1100	1100	120	1500
10	5250	5380	2350	....
11	....	....	280	1550
12	1900	2000	225	4000
13	1620	1550	300	2900
14	1000	1000	400	2450
15	3650	3700	3850	5220
16	800[1]	Red	80	....
17	60[1]	Pink	100	....
18	800[1]	Red	....	....
19	180[1]	Pink	....	....
20	4900	4900	2800	....

[1] Not acidity, but $CaCO_3$ present.

It will be noted that the potassium thiocyanate method agrees more closely with the Veitch ($Ca(OH)_2$) method than with the others. It is to be expected that the lime requirement would be higher by the potassium thiocyanate than by the potassium nitrate method because in the combined solution and metathesis both iron and aluminium are in solution, whereas only traces of iron are in solution by the latter method.

It was noted by Swanson, Latshaw and Tague,[1] in making a study of soil acidity by electrometric titration, that the lime requirement by the Hopkins method was usually lower than the electrometric method and "appeared too low when studied in connection with the known cropping conditions of the soil."

DETERMINATION OF CALCIUM CARBONATE ADDED TO SOIL

The method was tried on soils treated with varying limestone applications in pot culture work after a crop had grown for 4 mo. The results given in Table II were obtained:

TABLE II—AMOUNT OF LIMESTONE APPLIED AND RECOVERED FROM 14 LBS. OF SOIL
(Determined on 50-G. Sample)

SAMPLE		APPLIED Grams	FOUND Grams	DIFFERENCE Grams
1	Check	0	0	1300 Lbs. per Acre or 0.033 G. Required
2	Check — 1% $CaCO_3$	(0.5)	0.458	0.042
3	Check — 2% $CaCO_3$	1.0	0.858	0.142
4	Check — 3% $CaCO_3$	1.5	1.358	0.142
5	Check — 4% $CaCO_3$	2.0	1.833	0.167

The difference in amount of calcium carbonate recovered and applied may be due to imperfect mixing of the limestone with the soil or to exchange of bases taking place in the soil.

SUMMARY

1—The data presented seem to show that some iron and aluminium are present in an acid soil in an easily soluble condition and can be extracted by salts which are nearly neutral.

---

[1] *Soil Sci.*, **11** (1921), 144.

[1] *J. Agr. Research*, **20** (1921), 855.

2—The colored ferric thiocyanate changes to a colorless compound on the addition of a base, and the change takes place at a H-ion concentration of pH 5.5, which is thought to be the soil condition when the pink color just leaves.

3—The addition of a few drops of an alcoholic solution of logwood to the potassium thiocyanate extract from the soil indicates by the depth of the blue color the relative amount of aluminium in solution.

4—The limestone requirement by this method corresponds closely to the Veitch method.

5—The method seems to lend itself to the determination of either the acid or basic condition of a soil, and the soluble iron and aluminium found have been helpful in pointing to a source of some of the plant disease troubles.

Studies of the Availability of Organic Nitrogenous Compounds—Part I[1,2]

By C. S. Robinson, O. B. Winter and E. J. Miller

Michigan Agricultural College Experiment Station, East Lansing, Michigan

Several years ago there was started in this laboratory an investigation of the relation between the chemical constitution of organic nitrogenous substances and the availability of their nitrogen for plant nutrition. The objects of this work were two in number: (1) to ascertain whether or not any relation existed between chemical constitution and availability, and (2) either to devise a new method or to improve the present ones for measuring this availability. Both of these subjects are of importance because of the growing tendency to utilize all sorts of organic nitrogenous materials for fertilizer purposes.

Relation of Chemical Constitution to Availability

The fundamental chemical questions involved in the subject of availability have received considerable attention. Jodidi,[3] for instance, studied them in connection with the decomposition of amino acids and acid amides in the soil. He found that, of the simple aliphatic α-amino acids, the short chain glycine was more readily ammonified than the longer chain leucine and that the cyclic compound phenylalanine was more resistant to such action than leucine. He confirmed these results by experiments with glutaminic acid and tyrosine, and found that amino acid nitrogen is as readily ammonified in the soil as acid amide nitrogen. His work was done with simple amino acids, acid amides, and primary amines.

Kelley[4] went a step further and studied the decomposition of various proteins and other complex organic compounds, such as casein, dried blood, soy-bean cake meal, cottonseed meal, linseed meal, zein, and globulin from cottonseed meal. He found that about 60 per cent of the nitrogen in casein, about 50 per cent of that in dried blood and soy-bean cake meal, and approximately 30 per cent of that in cottonseed and linseed meals were easily convertible into ammonia. In studying the proportion furnished by different groups he found that the basic nitrogen was the most completely ammonified, with the amide and non-basic fractions variable, sometimes one and sometimes the other affording the larger amount as ammonia. In conclusion he said:

> It becomes apparent that all portions of the organic nitrogen in the different materials used as fertilizers and green manures are not equally susceptible to ammonification. It is evident, therefore, that chemical factors inherent in the nitrogen compounds themselves predetermine the availability to some degree.

Lathrop[5] has likewise investigated the ammonification of complex organic nitrogenous material. His first work was a study of the effect of "processing" on the organic nitrogen of fertilizer materials. He showed that such processing causes a more or less complete hydrolysis of the protein present in this raw material. This results in an increase in the soluble nitrogen with the formation of the usual products of such treatment. Later he made a thorough study of the decomposition of dried blood in the soil.[1] He found that over 79 per cent of the nitrogen in this material was ammonified during the 240 days of the experiment. He sums up the processes involved as follows:

> The ammonia produced during the decomposition of the dried blood was derived from (1) the hydrolytic cleavage of the proteins of the dried blood, as evidenced by the rapid vanishing of the amide compounds from the soil during the first 5 days of the experiment, and (2) from the decomposition of the products resulting from the hydrolytic cleavage of the proteins. Some of the ammonia produced during the first 2 or 3 days, when the hydrolysis of the proteins does not seem to have been very extended, may possibly have been due to the de-aminization of the ϵ-amino group of the lysine in the native proteins of the dried blood. With the exception of the amide compounds, lysine seems to have disappeared most rapidly and completely from the soil. The monoamino acids contributed about 89 per cent of their nitrogen to the formation of ammonia, and arginine and histidine each contributed about 83 per cent.

It is apparent from these researches that there is at least a strong possibility of a relation between chemical constitution and availability, although but little effort has been made to correlate this fact with the practical measurement of availability.

The invention of laboratory methods for determining the relative values of organic nitrogenous materials has proved attractive to many investigators, and a number of such methods have been proposed. Only two, however, the so-called neutral and alkaline permanganate methods, have shown themselves to be of sufficient value to continue long in general use. Both of them were developed rather empirically but nevertheless appear to give excellent comparative results from a practical viewpoint.

The Alkaline Permanganate Method[2]

Much work has been done upon this method by its originator, C. H. Jones,[3] who, while appreciating its shortcomings, has shown conclusively that it is valuable for differentiating in a broad way between high- and low-grade goods. One fault is that it does not give reliable results with vegetable ammoniates like cottonseed meal. This has been attributed by Jones to a high content of non-nitrogenous organic matter, a contention which is supported by results obtained with mixtures of high-grade products like dried blood and non-nitrogenous materials such as filter paper. Under these circumstances the availability of the nitrogen in the dried blood is lowered.

Another criticism that has been made[4] is that the conditions must be so carefully controlled that there is difficulty in getting concordant results. On strictly theoretical grounds this would be anticipated. In the first place it appears that the reaction which is being measured is an incomplete one and that it is still progressing rapidly at the time it is stopped. Hence any variation in time will cause a corresponding variation in results. It should also be observed that at the end of the distillation period the contents of the flask consist of the residue from 2.5 g. of $KMnO_4$ and 15.0 g. of NaOH in only about 25 cc. of water, giving a concentration of alkali which is very high and correspondingly effective in speeding up the reaction.

---

[1] Received February 25, 1921.

[2] Published as Journal Article No. 19 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

[3] Iowa Agricultural Experiment Station, *Research Bulletin*, **9** (1912).

[4] Hawaii Agricultural Experiment Station, *Bulletin* **39** (1915).

[5] U. S. Department of Agriculture, *Bulletin* **158** (1914).

[1] *Soil Sci.*, **1** (1916), 509.

[2] Association of Official Agricultural Chemists, "Methods of Analysis," revised to November 1919, **1920**, 11.

[3] Vermont Agricultural Experiment Station, 11th Annual Report, **1898**, 160; 12th Annual Report, **1899**, 137; 14th Annual Report, **1901**, 219; This Journal, **2** (1910), 308; **4** (1912), 438.

[4] Street, This Journal, **2** (1910), 311.

In spite of these facts it has been found possible in practice in this laboratory to obtain satisfactory results, although rather careful work is required. As will be shown in a later paper, it seems that in many cases the reaction involved actually does go almost to completion under the prescribed conditions, while in other cases the size of the sample used is such that any ordinary variation in conditions does not permit the evolution of sufficient ammonia to cause material error.

The present investigation of the alkaline permanganate method was approached as follows: First, a number of amino acids and acid amides, typical organic nitrogenous compounds of known constitution in which the nitrogen was combined in several ways, were treated with alkaline permanganate in the manner prescribed for the determination of the active insoluble nitrogen. This gave information regarding the action of this reagent on nitrogen in various types of combination. A similar series of experiments was then conducted with some of the better known proteins or substances containing them. Finally a number of samples of commercial base goods were examined: (1) by the alkaline permanganate method for availability, and (2) by the nitrogen partition method of Van Slyke.

ACTION OF ALKALINE PERMANGANATE ON AMINO ACIDS[1]

In Table I are given the results of the action of alkaline permanganate solution on some of the more common amino acids and other nitrogenous compounds. In the last column are given the number of atoms of nitrogen which are converted into ammonia. It will be observed that in the case of the monoamino acids with the amino group in the α position, *i. e.*, those showing monoamino nitrogen by the Van Slyke method, the nitrogen is all converted into ammonia.

TABLE I—PER CENT OF TOTAL NITROGEN, AMMONIFIED WITH PERMANGANATE

MATERIAL	Structural Formula	Total N in Substance	Available N Percent Substance	Available N Percent Total N	Atoms N Ammonified
Glycine	$NH_2{-}CH_2{-}COOH$	18.70	18.61	99.60	1
Glutaminic acid	$COOH{-}(CH_2)_2{-}CHNH_2{-}COOH$	7.58	7.25	95.60	...
Tyrosine	$OH{-}C_6H_4{-}CH_2{-}CHNH_2{-}COOH$	7.74	7.65	98.80	1
Arginine	$NH_2CNH{-}NH(CH_2)_3{-}CHNH_2{-}COOH$	32.19	17.42	54.15	2
Lysine	$NH_2CH_2{-}(CH_2)_3{-}CHNH_2{-}COOH$	19.18	7.88	41.07	0.8
Diphenylamine	$C_6H_5{-}NH{-}C_6H_5$	8.18	4.93	60.6	0.6
Naphthylamine	$C_{10}H_7{-}NH_2$	9.76	4.72	48.4	0.5
Urea	$NH_2{-}CO{-}NH_2$	46.50	7.50	16.1	0.3
			9.72	20.9	0.4
Asparagine	$COOH{-}CH_2{-}CHNH{-}CONH_2$	18.22	9.82	53.85	1+
Acetamide	CH_3CONH_2	21.90	19.81	90.50	0.9

The two amines, diphenylamine and napthylamine, were only partially converted.

Lysine[1] gave only slightly less than one of its atoms of nitrogen in ammonia form. From the fact that the α-amino groups in the other amino acids reacted quantitatively under the conditions of the determination one would probably be safe in assuming that it is this group which is removed from lysine. This is further supported by the fact that the ϵ-group reacts only slowly with nitrous acid.

That there is a certain parallelism between the sensitiveness of amino groups towards nitrous acid and alkaline permanganate solution is shown in the case of urea. This substance gave up less than half of its nitrogen during the period of digestion with alkaline permanganate solution. Complete decomposition of this compound with nitrous acid under the conditions of the Van Slyke method is obtained only after 8 hrs., in comparison with as many minutes for the quantitative removal of α-amino nitrogen from amino acids.

The results with asparagine indicate that this conduct is rather typical of acid amides in general, as an analysis of this compound by the permanganate method caused the splitting off of only one atom of nitrogen as ammonia. This presumably was the amino nitrogen, judging from the results with the α-amino acids. Acetamide, on the other hand, having only one atom of nitrogen in its molecule and this in the amide group, gave it all up under these conditions. The ammonification of acid amide nitrogen by alkaline permanganate solution may possibly be a function of the number of carbon atoms in the chain, as Jodidi obtained evidence that this is true with the ammonification of amino acids in soil.

The results in this table furnish a basis for predicting the conduct observed with arginine, which yielded only two of its nitrogen atoms as ammonia. From the results with other α-amino compounds we should expect arginine to give up its α-amino nitrogen easily. We might then anticipate that the other amino group would be split off, but Kutcher[2] has shown that under the influence of permanganate the molecule is split into ammonia, carbon dioxide, and guanidinebutyric acid. This last product is then broken up into guanidine and succinic acid. The guanidine is further hydrolyzed into ammonia and urea, liberating the second molecule of ammonia in the process, while the two nitrogen atoms in urea are but incompletely ammonified as shown above with that substance.

To ascertain the approximate rate of decomposition of those substances which were not entirely ammonified, the samples were subjected to further distillation after adding 150 cc. of water. The results are shown in Table II.

TABLE II—PER CENT OF TOTAL NITROGEN AMMONIFIED ON REPEATED DISTILLATIONS

MATERIAL	DISTILLATION 2nd	3rd	4th
Glycine	0.00	....	....
Glutaminic acid	0.23	0.00	....
Tyrosine	0.00	....	....
Diphenylamine	0.86	0.86	0.80
Naphthylamine	0.43	0.29	0.31
Urea	2.96	2.02	2.00

With the exception of the second molecule of ammonia from arginine, we are dealing with the simplest conditions possible. If the situation is not complicated by any such secondary decomposition it may be assumed that the liberation of ammonia is a comparatively simple reaction. The general conclusion which is apparent from the results is that primary aliphatic amino groups are quantitatively ammonified, while amides, cyclic compounds, and amino groups in other than the α positions are ammonified to a less extent. The results obtained by using this method on a complex such as a protein or a commercial ammoniate would be expected to yield all of the α-amino nitrogen from the free amino acids, either originally present or formed during the determination, together with a variable fraction of the nitrogen from other nitrogen-containing radicals.

---

[1] Denis [*J. Biol. Chem.*, **9** (1911), 365; **10** (1911), 73] studied the action of alkaline permanganate solution on glycine, cystine, alanine and tyrosine. He showed that some of the ammonia is oxidized to nitric acid but otherwise all in these compounds goes to ammonia.

[1] Zickgraf [*Ber.*, **35** (1902), 3401] used barium permanganate to oxidize lysine. He obtained hydrocyanic acid, oxalic acid, and succinic acid as decomposition products, together with a small amount of some substance which he supposed to be glutamic acid. It was isolated in quantity insufficient to identify. In the light of our work his supposition appears to be erroneous, since the amino group of this compound would probably have been split off by the barium permanganate.

[2] Benech and Kutscher, *Z. physiol. Chem.*, **32** (1901), 278; Kutscher, *Ibid.*, **32** (1901), 413.

In the case of such complexes, however, this variable fraction assumes first place in point of importance. It has been shown that practically all of the free NH_2 groups in native proteins consist of ϵ-amino groups of lysine and acid amide radicals of dibasic acids, both of which are evidently but incompletely ammonified. Consequently the interest shifts to the secondary decompositions or the *aminofication* stage of the process. There are many data available on the hydrolysis (aminofication) of proteins by acids and alkalies, and we could predict from *a priori* considerations that this reaction would progress rapidly under the strenuous condition of the permanganate method. We could not necessarily, however, expect it to go to completion as the total time required for the complete hydrolysis of protein material is several hours, while in the permanganate procedure the reaction is stopped at the end of 90 min. It is, therefore, an incomplete reaction. But this incomplete reaction is the phase that determines to a large extent the final results obtained, since, as has been shown above, the amino acids resulting from it are quite completely ammonified. This introduces into the method an element of uncertainty which largely determines its value. If the extent to which hydrolysis proceeds approximates the extent of formation of available nitrogen in the soil, the results obtained are indicative of the worth of the material. The further they deviate from this the more inaccurate they become.

There is, of course, the added factor of uncertainty in the incomplete ammonification of the other nitrogen radicals indicated above. This, however, is relatively unimportant, since the α-amino nitrogen comprises in the neighborhood of 70 per cent of the total nitrogen of most protein hydrolysates.

Were the action of permanganate strictly comparable to that of nitrous acid we should expect, upon complete hydrolysis, the ammonification by the permanganate of all of the monoamino nitrogen, one-half of the lysine nitrogen, one-third of the histidine nitrogen, one-fourth of the arginine nitrogen, and an uncertain fraction of the amide nitrogen. Kutcher's results, as well as our own, show that a secondary reaction ammonifies an additional atom of nitrogen from arginine and, with a reagent such as the permanganate solution used, such secondary reactions undoubtedly take place with other compounds as well. This makes possible only a general analogy between the effects of the permanganate solution and a reagent like nitrous acid which is fairly specific in its action. However, it is apparent that a similarity does exist in the case of several of the common proteins which were investigated with this point in view.

ACTION OF ALKALINE PERMANGANATE ON PROTEINS

Samples were digested with alkaline permanganate solution according to the official method, assuming all of the nitrogen to be insoluble. That portion ammonified was classed as active insoluble. Other samples were hydrolyzed with acid in the usual manner and the monoamino, basic or diamino and acid amide nitrogen determined. The basic amino fraction consists of one-fourth of the arginine, one-half of the lysine, and one-third of the histidine nitrogen. The sum of both the amino and acid amide fractions is given in the last column of Table III for comparison with the active insoluble nitrogen. The figures show that except in the case of gelatin the permanganate digestion causes the ammonification of a portion of the nitrogen greater than that represented by the total amino but less than that equal to the sum of the amino and acid amide fractions.

TABLE III—PER CENT OF TOTAL NITROGEN OF PROTEINS IN VARIOUS FORMS

	Total Nitrogen	Active Insoluble Nitrogen	Amido Nitrogen	Amino Nitrogen	Amido + Amino Nitrogen
Casein	13.83	73.25	10.82	69.00	79.82
Egg albumin	12.64	63.35	8.65	59.26	67.91
Glutin	13.60	70.30	21.48	57.52	79.00
Gelatin	15.15	62.00	1.48	59.18	60.66
Fibrin	14.76	75.15	8.52	69.53	78.05
Albumin from blood	11.81	71.20	7.54	66.81	74.35

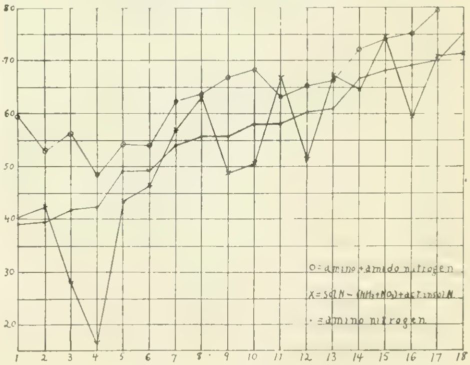
ACTION OF ALKALINE PERMANGANATE ON COMMERCIAL NITROGENOUS MATERIALS

It remained now to test out the above results with commercial materials. The total amide, mono-, and diamino acid nitrogen were determined after hydrolysis with acid, and the usual procedures were carried out in the estimation of available nitrogen by the alkaline permanganate method.

TABLE IV—PER CENT OF TOTAL NITROGEN OF FERTILIZERS IN VARIOUS FORMS

	Total Nitrogen	Soluble Nitrogen — (NH_3 + NO_3) + Active Insoluble	Amide Nitrogen	Amino Nitrogen	Amide + Amino Nitrogen
Peat (dried)	2.76	40.21	20.65	39.14	59.79
Peat (wet)	3.49	42.40	13.46	39.53	52.99
Pulverized sheep manure	2.34	28.20	14.53	41.88	56.41
Hay and silage	3.10	16.71	6.13	42.22	48.35
Fruit and vegetable	3.74	43.85	5.09	49.20	54.29
Bone meal	2.48	46.43	4.84	49.20	54.04
Animal tankage	4.40	56.94	7.95	54.31	62.26
Pure bone meal	3.12	62.81	8.01	55.76	63.77
Castorbean pomace	4.78	48.96	11.09	55.85	66.94
Cottonseed meal	6.73	50.51	10.33	58.09	68.42
Kazoo brand	2.32	66.81	5.17	58.18	63.35
Mixed-chrome uppers	9.88	51.22	4.76	60.32	65.08
Bone	3.05	67.21	5.24	60.98	66.22
Glue hair	8.49	64.55	5.89	66.77	72.66
Beef scraps	8.72	74.54	5.96	68.11	74.07
Animal tankage, II	4.62	59.30	5.84	69.26	75.10
Hair waste	14.07	70.85	9.52	70.00	79.52
Dried blood	14.01	71.31	6.56	75.23	81.79

Of the fractions obtained by the permanganate method the water-soluble fraction should consist of the ammonia and nitrate nitrogen, together with such soluble organic compounds as may be present, such as free amino acids, acid amides, urea, etc. The active insoluble portion should include that portion of the protein material which is hydrolyzed and ammonified in the course of the digestion. From the results with individual proteins and simpler compounds we should expect that the sum of the active insoluble and



water-soluble portions minus the nitrate and ammonia nitrogen would show the same relation to the amino and amide fractions as did the active insoluble portions of pure proteins. Table IV gives these figures, which are shown graphically in the figure, the values being plotted in order of ascending values of the amino nitrogen. The similarity in trend is very apparent. It could not, of course, be expected that the results would agree since, for reasons already pointed out, the active insoluble portion includes only part of the amino nitrogen and a variable fraction of the acid amide nitrogen.

Evidently the results with these materials do not show the same consistency as did those with pure proteins and the simpler compounds. In 50 per cent of the cases, hydrolysis was apparently incomplete, assuming that all amino nitrogen liberated during acid digestion is capable of being ammonified in the permanganate digestion. This is shown by the fact that the ammonia produced in the process was not equal in amount to the total amino nitrogen. In the other cases results analogous to those with proteins were obtained, *i. e.*, apparently all of the amino and part of the amide nitrogen was ammonified. These results are, nevertheless, in harmony with the considerations stated above, it having been pointed out that the reaction is still incomplete at the end of the digestion period in the permanganate method.

Discussion and Summary

In the light of the discussion in the earlier part of the paper, together with the experimental data, certain general statements regarding the availability of organic nitrogenous compounds seem justified. It is, of course, conceded that inorganic compounds of ammonia and nitric acid constitute a class of immediately available material. Assuming that the *ammonifying*, as distinguished from the *aminofying* or hydrolyzing, power of the alkaline permanganate solution is comparable to the action of soil agents, we may add to the nitrogen of the above members of the available class of compounds all amino nitrogen present in the form of α-amino acids and a portion of that nitrogen present as acid amides.

Then there is another class of compounds which we have called the *potentially available* class. It includes such substances as may be converted into members of the former class, and consists of a portion of the acid amides, the peptides, which can be hydrolyzed to amino acids, and primary and secondary amines. The peptides probably form the great bulk of this class so far as ordinary fertilizer materials are concerned. This class is the uncertain quantity in evaluating any material from the fertilizer standpoint. In some cases transformation into the available class is so easy and complete that there can be no practical distinction between the two. In other cases this process is so slow that the other extreme, *i. e.*, the unavailable class, is approached. Fundamentally, the problem of devising a method for the determination of the availability of organic nitrogen compounds is the invention of one which will properly estimate the rate of aminofication of the members of this class. Up to the present the permanganate methods have proved the most satisfactory. They are being studied further in the light of the work reported in this paper and the results will be published in the near future.

The Chemical Constitution of Soda and Sulfate Pulps from Coniferous Woods and Their Bleaching Qualities[1]

By **Sidney D. Wells**

U. S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisconsin

In looking for a solution for the periodical shortage of raw materials for paper manufacturing, the investigator soon realizes the existence of the large and widespread supplies of wood too resinous for use in the sulfite process, and too resinous, dark colored, or hard for the manufacture of satisfactory mechanical pulp. Of all our standing timber only 3 per cent, existing in the Lake and Northeastern states, is available for use as a source of supply for the manufacture of over 70 per cent of our wood pulp production. In the same areas and in the southern states within a reasonable distance of the important publishing centers, occur stands of various species of pine, tamarack, and other coniferous woods amounting to 20 per cent of the total stand in the United States. They possess a very satisfactory fiber, but can be economically pulped only by alkaline processes, such as the soda or sulfate, by which the resinous matter is readily rendered soluble. Unfortunately, soda or sulfate pulps from coniferous woods are difficult to bleach to a satisfactory degree of white, and only relatively small amounts are produced for special purposes. Even spruce, which is used in large quantities in the manufacture of bleached pulps by the sulfite process, yields a soda or sulfate pulp about as difficult to bleach as longleaf pine or tamarack. Many investigators have attributed this to the presence of impurities such as lignin, but the writer has long felt that it is due to coloring matter present in the wood or produced during digestion, which is very small in amount but of high tinctorial power. In fact, it has been felt that sulfate pulps from the pines, spruces, and firs (even though cooked for strength and dark brown in color) more nearly approach cotton cellulose in chemical or physical characteristics than well-cooked sulfite pulps from the same wood. Studies were therefore undertaken to ascertain the chemical characteristics of typical soda and sulfate pulps from white spruce which were cooked under carefully regulated and known conditions, and also of portions of the same pulps bleached to various degrees.

Preparation of Pulps

The pulps were cooked in the semicommercial tumbling digester in use at the Forest Products Laboratory which has a capacity of 100 lbs. of dry pine chips, or a production of from 40 to 50 lbs. of bone-dry pulp per charge.[1] In Table I are presented the cooking conditions and yields of pulp obtained.

The bleached pulps were prepared from the unbleached pulp described above by bleaching with definite amounts of bleaching powder solution at 100° F. in glass vessels provided with mechanical stirrers. The bleaching operation in each case was continued until just a trace of active chlorine remained, as shown by starch iodide indicator. The pulps were then washed free from bleach residues, pressed, and allowed to dry by exposure to the air at 70° F. They were then stored in airtight fruit jars until needed. The amounts

---

[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[1] Kress, Wells and Edwardes, "The Equipment and Operation of an Experimental Pulp and Paper Laboratory," *Paper*, **26**, No. 13 (1919), 11; *Pulp Paper Mag. Can.*, **18**, No. 23, 588.

TABLE I

		Cooking Liquor					Cooking Conditions					
Cook No.	Kind	Volume per 100 Lbs. Dry Chip Gal	Concentration NaOH Grams per Liter	Concentration Na_2S Grams per Liter	Chemicals per 100 Lbs Dry Chips NaOH Lbs	Chemicals per 100 Lbs Dry Chips Na_2S Lbs	Maximum Time Reaching Pressure Hrs.	Time at Maximum Pressure Hrs	Maximum Steam Pressure Lbs. per Sq In	NaOH in Liquor at End of Cook Lbs.	Yield of Dry Pulp per Cook Per cent	Bleaching Powder Necessary to Bleach to Standard White
2	Well-cooked soda pulp........	31.2	118.0	....	30.6	..	1.75	7.00	100	8.8	33.8	23
3	Ordinarily cooked soda pulp	26.8	98.5	....	22.0	...	4.00	3.50	100	3.7	42.8	60
4	Well-cooked sulfate pulp.......	32.6	85.4	22.0	23.2	6.0	1.50	3.50	100	10.0	39.0	18
5	Ordinarily cooked sulfate pulp.	34.8	55.1	13.6	16.0	4.0	2.25	3.50	97	3.0	48.2	50

[1] Standard white was the color at which larger amounts of bleaching powder solution failed to improve the color.

of bleaching powder (35 per cent available chlorine) used in producing each of the bleached pulps and the yields of bleached pulp obtained are given in Table II.

TABLE II

Soda Pulp			Sulfate Pulp		
Cook No.	Bleaching Powder Per cent	Yield Per cent	Cook No.	Bleaching Powder Per cent	Yield Per cent
2	0	33.8	4	0	39.0
	7	32.8		6	38.7
	15	32.5		15	39.2
3	0	42.8	5	0	48.2
	12	41.9		10	47.6
	20	40.7		25	46.2

The figures for bleaching powder are based on the bone-dry weight of the unbleached pulps, while the figures for yields are based on the bone-dry weight of the original wood chips.

CHEMICAL TESTS

Comprehensive chemical studies were made on each of the pulps indicated above by Messrs. D. E. Cable, M. W. Bray, and J. A. Staidl, under the supervision of Dr. S. A. Mahood. The chemical constants determined were those employed by Schorger[1] in the analysis of certain American woods, together with certain additional tests such as lignin and α-, β-, γ-cellulose of the chlorinated residue. Their value is dependent on operating under closely regulated conditions, and a complete description of the methods used and directions for operating will be given in an article by Messrs. Bray and Staidl entitled "Methods of Analysis of Wood Pulps by the Forest Products Laboratory."

In Table III are given the results of the determinations of moisture, ash, cold-water-soluble, hot-water-soluble, alkali-soluble, acetic acid by hydrolysis, and ether extract.

TABLE III
(Values given in per cent)

Cook No.	Process	Bleaching Powder, 35 Per cent Available Chlorine	Moisture	Ash	Cold-Water-Soluble 48 Hrs	Hot-Water-Soluble 3 Hrs.	Alkali-Soluble, 1 Per cent NaOH, 1 Hr.	Acetic Acid by Hydrolysis	Ether Extract
2	Soda	0	3.48	0.90	1.27	0.62	2.46	0.06	0.41
		7	4.94	0.91	0.51	0.08	3.40	0.06	0.52
		15	5.66	1.22	0.45	0.18	9.81	0.04	0.76
3	Soda	0	3.91	1.12	0.71	0.26	2.81	0.07	0.49
		12	6.26	0.92	0.58	1.07	4.93	0.06	1.10
		20	5.79	0.90	1.27	1.21	6.92	0.04	0.71
4	Sulfate	0	3.64	1.01	1.23	0.82	2.18	0.06	0.63
		6	5.74	0.83	0.00	0.00	2.28	0.03	0.89
		15	5.49	1.21	0.00	0.00	8.51	0.04	0.93
5	Sulfate	0	4.89	1.16	1.25	0.40	2.62	0.10[1]	1.65
		10	6.04	1.27	0.59	0.00	3.61	0.04	1.42
		25	5.97	1.40	1.23	0.91	14.02	0.04	1.10
White spruce wood				0.2	2.3	3.8	8.8	1.6	1.3

[1] Result high and check determination was unfortunately lost.

The results of ash determinations indicate, as would be expected, that most of the ash in the wood is retained by the pulp, in addition to certain amounts of ash from the cooking liquor, bleach liquor, and water retained through unavoidable irregularities in washing.

The results of both cold- and hot-water-soluble determinations indicate soluble impurities in negligible amounts, due to slight differences in washing the pulps during the manufacturing operation.

The solubility of the unbleached pulps in 1 per cent sodium hydroxide solution are very low, which would be expected upon consideration of the fact that the pulping operation is an alkaline digestion. The bleaching operation, however, renders considerable amounts of the pulps soluble in alkali. The amount of alkali-soluble constituents formed increases very slowly with small amounts of bleach, but, after 6 per cent of bleach is passed with well-cooked pulps and 12 per cent with kraft pulps, the increase in solubility is very rapid, indicating that this test would be useful to detect the occurrence of over-bleaching. The presence of alkali-soluble constituents long before satisfactory color is obtained indicates that the cellulose material is being degraded as well as the coloring matter, and suggests the desirability of improved methods of bleaching.

The extremely small amount of acetic acid by hydrolysis indicates the removal during digestion of a large proportion of what acetyl groups occur in spruce.

The ether extract, consisting of the waxes, fats, resins, etc., is extremely low in all the pulps except those from Cook 5. In Cooks 2, 3, and 4 there seems to be a tendency to form ether-soluble constituents to a slight extent by bleaching. The differences, however, are small, and to a large degree may have been introduced in shredding the pulp in a mechanical shredder. In Cook 5 the relatively high results seem to indicate that the difficulty of washing what would be termed a semi-cooked pulp has resulted in insufficient washing.

The results of the remaining determinations are given as follows:

Pentosan, methylpentosan, furfuroids, methoxy groups, cellulose, and lignin. (Table IV.)

α-, β-, and γ-cellulose, pentosan, methylpentosan, and furfuroids in the chlorinated residue reported as cellulose. (Table V.)

TABLE IV
(Values given in per cent)

Cook No.	Process	Bleaching Powder, 35 Per cent Available Chlorine	Pentosan	Methylpentosan	Furfuroids	Methoxy Groups	Cellulose	Lignin (Non-cellulose)
2	Soda	0	3.82	1.25	2.54	0.47	96.20	2.11
		7	3.98	1.66	2.76	0.26	97.16	2.66
		15	4.09	0.63	2.54	0.29	97.05	2.22
3	Soda	0	7.77	1.14	4.82	0.89	93.17	4.03
		12	8.24	1.18	5.09	0.57	94.26	5.86
		20	8.20	1.35	5.12	0.32	94.77	4.55
4	Sulfate	0	6.05	1.07	3.79	...	96.17	1.88
		6	7.67	1.35	4.51	0.24	95.68	3.43
		15	7.17	1.62	4.22	0.18	95.40	2.64
5	Sulfate	0	10.04	0.92	6.09	0.68	94.56	3.39
		10	10.07	0.64	6.05	0.26	94.00	5.53
		25	9.90	0.85	6.00	0.25	94.56	4.04
White spruce wood			11.9	1.9	...	5.3	58.6	28.3

The pentosan content as indicated by the pentosan, methylpentosan, and furfural determinations is reduced by alkaline digestion. The soda pulps are lower in pentosan than the sulfate, but when the yields of pulp are considered the sulfate process, with the same reduction of yield, produces a pulp lower in pentosan. Bleaching does not reduce the value

---

[1] THIS JOURNAL, 9 (1917), 556.

TABLE V
(Values given in per cent)

Cook No.	Process	Bleaching Powder, 35 Per cent Available Chlorine	In Cellulose Alpha	In Cellulose Beta	In Cellulose Gamma	Pentosan	Methylpentosan	Furfuroids
2	Soda	0	80.30	13.27	6.43	3.42	1.54	2.33
		7	55.93	34.22	9.85	3.87	1.88	2.71
		15	51.50	37.80	10.70	3.41	1.92	2.48
3	Soda	0	85.66	7.81	6.53	7.31	1.52	4.59
		12	60.57	34.19	5.24	7.45	1.33	4.63
		20	53.01	35.07	11.92	6.80	1.50	4.32
4	Sulfate	0	81.80	10.31	8.07	5.81	1.62	3.85
		6	72.20	18.72	9.08	6.95	1.01	4.28
		15	62.95	26.90	10.15	6.20	0.97	3.84
5	Sulfate	0	84.20	6.31	9.49	9.96	1.29	6.10
		10	64.70	23.98	11.32	8.30	1.70	5.26
		25	56.87	31.55	11.58	8.46	1.46	5.27
White spruce wood			63.6	10.4	26.1	...	...	...

given by these tests, but since oxycellulose[1] also yields furfural the indications of these tests for bleached pulps are not so illuminating.

The methoxy content of both soda and sulfate pulps are very low and indicate the absence of lignin. Sulfate pulps are much purer than soda pulps in this respect, and even Cook 5, which would be regarded as only semi-cellulose by European authorities. is remarkably low. Bleaching reduces the amount of methoxy groups still more.

The yields of cellulose by the chlorination method of Cross and Bevan are of particular interest because the paper maker is interested in a white fibrous product of certain physical properties and resistant to the action of the atmosphere or light. Whether the fiber has the same constitution as cotton cellulose does not concern him. The residues obtained from the chlorination method meet his requirements, and if the laboratory procedure could be extended to commercial operation without undue cost it undoubtedly would be used. The results of this determination indicate that both soda and sulfate pulps are capable of giving very high yields of bleached fiber of most satisfactory white. The sulfate pulps give much higher yields, however, when the original weights of wood are considered. The lignin determinations also indicate that sulfate pulps are much superior to soda pulps when the weight of wood used is considered. The fact that mild bleaching increases the lignin determinations while further bleaching reduces them is interesting, and indicates that addition products are probably first formed and are later removed, and suggests the feasibility in commercial operation of removing them before the bleaching operation is continued. The α-, β-, and γ-cellulose determinations on the residue from the cellulose determination indicate that the α- or most resistant portion of the residue is diminished, the more drastic the cooking conditions or the further the bleaching is carried. The β-portion is increased by increased digestion, and also by bleaching. The γ-portion seems to be reduced by more drastic cooking but bleaching tends to increase it. The reduction of the amount of so-called α-cellulose by both alkaline digestion and bleaching made it appear desirable to make similar determinations on the unbleached pulps. These were later made on all but Cook 4, of which none remained. The results for soda pulps were as follows:

	α	β	γ
Cook 2	78.20	5.46	16.54
Cook 3	85.25	7.15	7.60

The well-cooked soda pulp is lower in α- and β-cellulose than the residue from the same on chlorination, but much higher in γ-cellulose, on account of the fact that the various steps in the chlorination method probably dissolve a considerable proportion of it. With the raw soda pulp, Cook 3, the results differ much less from the residue from chlorination. The α-determination on the unbleached pulp of Cook 5, the raw sulfate cook, was 86.50 per cent; considerably higher than the same for the residue from chlorination and the highest of any in the series. Unfortunately an accident prevented the determination of the β- and γ-constituents. The data, as far as they go, indicate the greater effectiveness of the sulfate process in isolating the resistant fibrous constituents of wood with the least loss of material.

The pentosan, methylpentosan, and furfural determinations on the residue from chlorination indicate that the chemical operations through which the pulp has passed in this method has reduced the constituents represented above but little, if at all. It is, however, further evident that, from the standpoint of the manufacture of bleached pulp, the presence of these constituents may be ignored.

The study of the chemical data makes it appear evident that there is not any substance in considerable quantity that causes the color or difficulty in bleaching soda or sulfate pulps. A comparison of the bleachability and yields of the pulps under discussion will further emphasize the point.

Process	Cook No.	Yield Per cent	Bleach Required Per cent	Yield Chlorinated Residue Unbleached Pulp Per cent	Bleached Pulp Per cent
Soda	2	33.8	23	32.5	32.0
Soda	3	42.8	60	39.8	40.0
Sulfate	4	39.0	18	37.5	39.0
Sulfate	5	48.2	50	45.6	44.5

In the case of Cook 5 a yield of 44.5 per cent of bleached pulp was possible, using 50 per cent of bleaching powder. In order to obtain a pulp that could be bleached with 18 per cent of bleaching powder a reduction of yield to 39 per cent was necessary. The residue obtained by chlorination was 45.6 per cent in the former case, against 37.5 per cent in the latter. It is apparent that in order to produce a pulp that could be bleached with reasonable amounts of bleaching powder, 8.1 per cent of white, fibrous cellulose material has been destroyed, or over 21 per cent of the pulp obtained.

The work clearly indicates that the problem of using sulfate or soda pulps for the better grades of light colored papers lies in the bleaching rather than in the cooking operation. The use of caustic soda alone in digestion is also shown to be much more inefficient in resolving wood to bleachable pulp than the use of caustic soda with the addition of some reducing compound, such as sodium sulfide. The chemical data furthermore emphasize the desirability of carrying on the cooking operation as mildly as possible and leaving as much for the bleaching operation as can be accomplished without degrading the cellulose.

The amount of material that must be removed is extremely small and is clearly of the nature of a dye. The procedure used in making analytical determinations of cellulose would be ideal but unfortunately cannot be considered on a commercial scale. Combinations of oxidation and reduction with washing between steps, have been tried with promising results. An account recently published[1] of some work done on loblolly pine and red gum describes how the bleach consumption of sulfate pulps obtained with a yield of from 40 to 42 per cent was reduced from 30 per cent to 15 per cent with whiter pulp, by dividing the bleaching operation into two steps and washing between each step. Yields of 45 per cent have since been bleached with 18 per cent of bleaching powder, using the same methods. These results give additional evidence to the value of modifying the bleaching operation and it is believed that further work now in progress will make possible higher yields with satisfactory quality.

---

[1] Browne, "Handbook of Sugar Analysis," p. 452.

[1] "Book Paper from Southern Pines and Gums," *Paper*, **27**, No. 11 (1920); *Paper Trade J.*, **71**, No. 22, 34; *Southern Lumberman*, **98**, No. 1318, 47; *Paper Ind.*, **2**, 1527.

Conclusions

The chemical characteristics of soda and sulfate pulps indicate that they are a very pure form of wood cellulose and capable of high yields of white fibrous and resistant material.

The sulfate process is much more efficient than the soda process in yielding a bleachable pulp from coniferous wood.

The coloring matter in pulps is of the nature of a dye and can be removed without materially reducing yields. Most of the action in cooking to reduce bleach consumption is to dissolve and degrade the cellulose.

Modifications in bleaching methods give promise of greater results than modifying cooking methods.

Modifications in which the bleaching operation was divided into two steps, with washing between steps, cut the bleach requirement in two.

Pulps of better quality, both from physical and chemical considerations, are obtained by cooking the wood as little as possible in isolating the fibers and by accomplishing as much of the burden of purification as possible in the bleaching and washing operations.

The Determination of Vanadium and Chromium in Ferrovanadium by Electrometric Titration[1]

By G. L. Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright

Midvale Steel & Ordnance Co., Nicetown Plant, Philadelphia, Pennsylvania

The object of this paper is to describe a method for the determination of vanadium in ferrovanadium not subject to interference by chromium, which is so often present. Kelley and Conant[2] described the electrometric titration of vanadium following oxidation with ammonium persulfate and silver nitrate, but the method did not provide against the possible presence of chromium. Kelley and the collaborators[3] above named described a method for the selective oxidation of vanadium in steel in the presence of chromium, using nitric acid as an oxidizing agent. At that time, however, we were not prepared to recommend the application of our procedure to the determination of vanadium in ferrovanadium. Since then its application to the analysis of this alloy has been studied.

Preliminary Experimental Work

DETERMINATION OF VANADIUM IN AMMONIUM VANADATE—A large volume of solution was prepared from ammonium vanadate described by the maker as C. P. This was analyzed by two methods. In the first, the vanadium was determined by titrating the solution with ferrous sulfate and dichromate, taking as the end-point the point of greatest change in the oxidation-reduction potential. The potassium dichromate solution was made from a C. P. salt which had been recrystallized and fused. It was also compared through the ferrous sulfate with permanganate which had been standardized against sodium oxalate. The average difference between these standardizations was less than one part in one thousand. In the second method, 100 cc. of the ammonium vanadate solution were placed in a flask, with an equal volume of water and 5 cc. of sulfuric acid (sp. gr. 1.58), and treated with sulfur dioxide for 20 min. at the boiling temperature. The excess of sulfur dioxide was removed by passing purified carbon dioxide through the still boiling solution for an additional 20 min. Two hundred cc. of a boiling water solution containing 50 cc. of sulfuric acid (sp. gr. 1.58) were next added, and the mixture was titrated hot with 0.05 *N* permanganate using the potentiometric end-point. Eight determinations by the first method gave 0.1273 and 0.1274 g. of vanadium in 100 cc. of solution, the average result being nearer 0.1273. The solutions titrated with permanganate after sulfur dioxide reduction did not agree so well. The results ranged from 0.1269 to 0.1275, averaging 0.1272.

The condition most favorable to titration with ferrous sulfate is an acid concentration of about 50 cc. of sulfuric acid (sp. gr. 1.58) in a volume of 350 cc. at a temperature of 5° C. Under these circumstances the change in potential for 0.05 cc. of the ferrous sulfate solution (23 g. ferrous ammonium sulfate in one liter) is about 50 mv. at the end-point. When the vanadyl sulfate is titrated at 80° C. with permanganate in a similar acid concentration, the change of potential is about 60 mv. Under these conditions the color of permanganate is not visible until about 0.20 to 0.25 cc. more of the permanganate solution has been added. The poorer quality of the work done with permanganate may be due to the incompleteness of the reaction between the permanganic acid and vanadyl sulfate, and the results are, doubtless, affected by the exposure of the hot solution to air during titration.

NITRIC ACID OXIDATION—The solution of vanadyl sulfate, standardized as above, was used to check further the degree of oxidation effected upon vanadyl salts by nitric acid. In our earlier paper on the selective oxidation of vanadyl salts by nitric acid in the presence of chromic salts, it was suggested that the vanadium be considered approximately 99 per cent oxidized. Our more recent work leads to the belief that the degree of oxidation is more nearly 99.5 per cent. With the object of simulating conditions which would obtain if the work were done upon ferrovanadium, solutions were prepared containing 0.3 g. of pure iron, 0.1273 g. of vanadium as ammonium vanadate, 25 cc. of sulfuric acid (sp. gr. 1.58), 40 cc. of nitric acid (sp. gr. 1.40), and water enough to make the total volume 200 cc. The iron was first dissolved in the sulfuric acid and water in the presence of the ammonium vanadate, thus reducing the latter to vanadyl sulfate. The mixture was boiled for 1 hr., at such a rate that the volume was 100 cc. at the end of the period. It was then cooled to 5° C. and titrated electrometrically with ferrous sulfate and potassium dichromate. Out of twenty-four determinations made, the value found for percentage oxidation was 99.3 in four cases, 99.5 in eleven, 99.6 in six, and 99.7 in three.

The average was 99.5 per cent oxidation, with a maximum variation of 0.2 per cent above and below.

We have previously shown[1] that chromium is not oxidized under these conditions.

We have made a further investigation of the effect of conditions upon the oxidation of vanadium by nitric acid, but inasmuch as our results were largely negative, they need not be described in detail. Oxidations conducted in flasks at the boiling temperature, with air passed through for 6 hrs., did not show consistently higher oxidation than solutions boiled 1 hr. in beakers covered with watch glasses. When air was excluded, the results were slightly lower.

Method for Determining Chromium and Vanadium in Ferrovanadium

Dissolve 3 g. of ferrovanadium in 75 cc. of nitric acid (sp. gr. 1.13). When solution is nearly complete, add 10 cc. of hydrochloric acid (sp. gr. 1.20). When the amount of silicon is large, it may be convenient to add a few drops of

---

[1] Received April 13, 1921.

[2] *J. Am. Chem. Soc.*, **38** (1916), 349.

[3] This Journal, **11** (1919), 632.

[1] *Loc. cit.*

hydrofluoric acid to bring about solution. Next add 50 cc. of sulfuric acid (sp. gr. 1.58) and evaporate until fumes appear, to remove nitric and hydrochloric acids, and to complete the decomposition of vanadium carbides. The insoluble residue after this treatment is generally small and consists chiefly of aluminium oxide. Ordinarily no loss of vanadium occurs if it is disregarded, but it may be dissolved in water after fusion with sodium peroxide. The alkaline solution so obtained should be boiled for at least 15 min. to remove hydrogen peroxide. The solution may then be acidified with a slight excess of sulfuric acid and added to the main filtrate. This solution is then cooled and made up to a volume of 1000 cc. One hundred cc. portions of this solution, corresponding to 0.3 g., are convenient quantities for subsequent work.

DETERMINATION OF VANADIUM AND CHROMIUM—To a 100-cc. portion add 25 cc. of sulfuric acid (sp. gr. 1.58) and water enough to make the volume 300 cc. Heat the solution to boiling and add 20 cc. or more of a 10 per cent solution of ammonium persulfate and 10 cc. of a 0.25 per cent solution of silver nitrate. Boil the solution at least 10 min. to oxidize the vanadium and decompose the excess of ammonium persulfate. If there is no manganese in the ferrovanadium, some should be added, as the persistence of the color of permanganic acid is a good indication that the amount of ammonium persulfate added has been sufficient to complete the oxidation of all chromium and vanadium. After 10 min. boiling, add 5 cc. of hydrochloric acid (1 : 3), and continue the boiling 5 or 10 min. longer. In this way the permanganic acid is completely destroyed without reducing either chromium or vanadium. After the addition of a further 25 cc. of sulfuric acid and cooling to 5° C., the solution may be titrated electrometrically. It is convenient to use for the titration the solutions used in titrating chromium in steel. As described in the previous paper, these are made by dissolving 2.828 g. of potassium dichromate in water to make 1000 cc., and by dissolving 23 g. of ferrous ammonium sulfate and 100 cc. of sulfuric acid (sp. gr. 1.58) in enough water to make 1 liter. The dichromate solution is used for reference and the ferrous sulfate solution compared with it electrometrically at the time the work is done. When a high degree of accuracy is desired and the conditions under which the work is carried out require it, the dichromate should be purified and fused before weighing. Each cubic centimeter of this dichromate solution is equivalent to 0.001 g. chromium or 0.002943 g. vanadium. When the ferrovanadium oxidized as described above is titrated with ferrous sulfate and dichromate, both chromium and vanadium are titrated. Multiplying by 2.943 and dividing by 3 gives the apparent percentage of vanadium, which includes both vanadium and chromium.

DETERMINATION OF VANADIUM—The vanadium is determined in a separate 100-cc. portion. During the evaporation of the nitric acid solution with sulfuric acid, a slight oxidation of chromium may have occurred. It is, therefore, desirable to add a few cc. of ferrous sulfate solution to reduce this. After a few minutes boiling, add 20 cc. of sulfuric acid (sp. gr. 1.58), and 40 cc. of nitric acid (sp. gr. 1.40), together with enough water to make the volume 200 cc. Place a label on the beaker marking the 100-cc. level, and boil at such a rate that the volume is reduced to 100 cc. in 1 hr. Dilute the solution with ice water and cool to 5° C. to titrate. Divide the titration result by 995 and multiply by 1000. Divide the product by 3 and multiply by 2.943. This gives the actual percentage of vanadium.

CHROMIUM BY DIFFERENCE—By subtracting the actual percentage of vanadium from the percentage representing both chromium and vanadium we obtain a figure corresponding to chromium but expressed in terms of vanadium. Dividing this by 2.943 gives the percentage of chromium.

The use of the factor 2.943 may be avoided if 2.883 g. of potassium dichromate are used to prepare the solution. In this case each cc. corresponds to 1 per cent of vanadium when the sample titrated contains 0.3 g. of the ferro-alloy.

APPLICATION OF METHOD

The application of this method to the analysis of two samples of ferrovanadium known to contain chromium gave the following results:

	Chromium and Vanadium as Vanadium		Vanadium	
SAMPLE	Per cent	Average	Per cent	Average
A	41.29, 41.32, 41.34	41.32	33.05, 33.13, 33.09	33.09
B	48.29, 48.35	48.32	43.30, 43.36, 43.40	43.35

By calculation from the averages, Sample A contained 2.80 per cent of chromium, and Sample B contained 1.61 per cent.

To check the accuracy of this method of determining chromium in ferrovanadium, a procedure which separated most of the vanadium was devised. It had the advantage of permitting work with a much larger amount of chromium in the presence of a greatly diminished percentage of vanadium. For this purpose 1-g. samples of ferrovanadium were dissolved in hydrochloric acid (sp. gr. 1.10), and oxidized with nitric acid. The solution was evaporated to a sirupy consistency, when a second portion of hydrochloric acid was added and the evaporation repeated. Iron was extracted from this with ether, and the aqueous solution evaporated with sulfuric acid until fumes appeared. It was then diluted to 160 cc., and 40 cc. of nitric acid (sp. gr. 1.40) were added. Boiling this solution under the prescribed conditions oxidized nearly all of the vanadium and no chromium. To the cool solution, sodium carbonate was added to precipitate iron and chromium, along with some manganese and a small amount of vanadium. The precipitate was washed and dissolved in nitric acid and a little water. The resulting solution was made up to a volume of 200 cc. after the addition of 40 cc. of nitric acid (sp. gr. 1.40), and 25 cc. of sulfuric acid (sp. gr. 1.58). After a second oxidation of vanadium by boiling, the chromium was again precipitated. This precipitate still contained vanadium, but only in a very small amount. It could have been completely removed by oxidizing the chromium with ammonium persulfate and precipitating the vanadium with uranium, as described elsewhere by us.[1] This did not seem necessary, and we, therefore, resorted to the easier procedure of determining the amount of vanadium present. The vanadium in the precipitate was oxidized with nitric acid in the usual way, and titrated with ferrous sulfate. The amount of vanadium so found varied with different samples, but averaged about 0.4 per cent. After titrating the vanadium, each solution was evaporated until sulfuric acid fumes appeared, after which it was diluted and both vanadium and chromium were oxidized with ammonium persulfate. The amount of chromium was large enough to require about 17 to 30 cc. of our ferrous sulfate solution for its titration, thus permitting a very accurate determination of combined chromium and vanadium. By subtracting the vanadium previously determined on each portion from the total of chromium and vanadium, new figures were obtained for the chromium present. In Sample A, chromium was found as 2.79, 2.77, and 2.77 per cent, which is in good agreement with 2.80 found by the first method. Sample B gave 1.62, 1.61, and 1.59 per cent, against 1.61 previously found.

SUMMARY

1—The authors have confirmed the identity between the electrometric end-point value obtained by titrating vanadium with ferrous sulfate and by titrating pure solutions of vanadyl sulfate with permanganate when suitable blanks are used in the later titration.

---

[1] THIS JOURNAL, **11** (1919), 632.

2—It is demonstrated that the oxidation of vanadium by nitric acid under a fixed set of conditions gives a very regular degree of oxidation.

3—It has been previously shown that chromium is not oxidized under the conditions described.

4—A method has been developed for the determination of vanadium in ferrovanadium containing chromium.

5—The authors have shown that the amount of chromium can be determined with accuracy from the difference between the titrations after oxidation with silver nitrate and ammonium persulfate and after oxidation with nitric acid.

6—Results have been given showing the chromium obtained after separating nearly all of both vanadium and iron.

Effect of Variation in Analytical Constants of Linseed and Soy-Bean Oils upon the Quantitative Determination of Linseed Oil in Mixtures of the Two Oils by Means of the Iodine and Hexabromide Numbers of the Fatty Acids[1]

By Edward A. Tschudy

E. I. du Pont de Nemours & Co., Philadelphia, Pennsylvania

In a recent paper[2] Bailey and Baldsiefen have published results for the quantitative determination of linseed oil in mixtures of linseed and soy-bean oils, by a modified method for the determination of the hexabromide number of the fatty acids. It is possible, from the results there enumerated, to show the relation existing between the iodine numbers and the hexabromide numbers of the fatty acids of such mixtures, and to ascertain the error introduced into a determination when oils having constants differing from those used by Bailey and Baldsiefen in their investigation occur in mixtures, the iodine or hexabromide numbers of which are compared with Tables III or IV of their paper to ascertain the percentage of linseed oil present in the mixtures.

RELATION BETWEEN IODINE NUMBER AND PERCENTAGE OF LINSEED OIL IN MIXTURES

By plotting the iodine numbers of the mixtures in Table III (Bailey and Baldsiefen) against the per cent of linseed oil (Graph I), the plotted points lie on a straight line, the general equation of which is

$$y = \frac{x - b}{m}.$$

For this case, y is the per cent of linseed oil in the mixture, b is the iodine number of the pure soy-bean oil in the mixture, x is the iodine number of the mixture, and m is the cotangent of the angle which the line makes with the x-axis. The iodine numbers of the oils used by Bailey and Baldsiefen in their work have not been recorded, but the linseed oil used probably had an iodine number of 179, and the soy-bean oil an iodine number of 135.5. Substituting these constants in the general equation it becomes

$$y = \frac{x - 135.5}{0.435}. \qquad (1)$$

Comparing the calculated values for the per cent of linseed oil in the mixtures with the per cent actually present, by substituting the determined iodine numbers in Equation 1, we find:

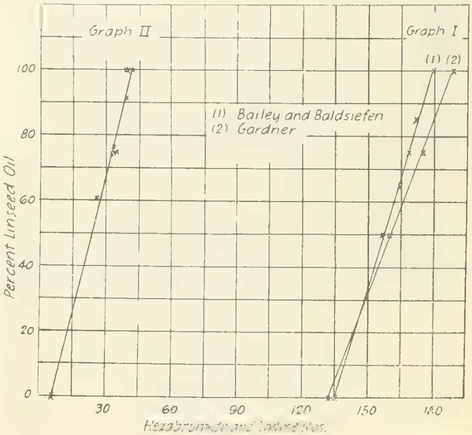
Mixture						
Linseed Oil Per cent	Soy-Bean Oil Per cent	Iodine Number Determined	Iodine Number Corrected	Linseed Oil Present Per cent	Linseed Oil Calculated Per cent	Percentage Difference
85	15	171.9	172.5	85	83.8	—1.2
75	25	168.0	168.1	75	74.7	—0.3
65	35	164.2	163.8	65	66.1	+1.1
50	50	...	157.3	50	...	...

The difference between the calculated percentage of linseed oil in the mixtures and the percentage actually present is very small, and within the limit of experimental error, which, for the iodine number, is usually ±0.5 unit.

This can be shown by substituting in Equation 1 the per cent of linseed oil present in the mixture and computing the corrected iodine number, as tabulated.

RELATION BETWEEN HEXABROMIDE NUMBER OF THE FATTY ACIDS AND THE PERCENTAGE OF LINSEED OIL IN THE MIXTURES

By plotting the hexabromide numbers of the fatty acids in Table IV (Bailey and Baldsiefen) against the per cent of linseed oil present in certain mixtures designated as Samples 793 to 811 (Graph II), the plotted points lie on a straight line similar to the iodine number-linseed oil curve, and have a similar general equation. For this line y is the per cent of linseed oil in the mixture, x is the hexabromide number of the fatty acids, b is the hexabromide number of the pure soy-bean oil in the mixture, and m the cotangent of the angle made by the line with the x-axis. The linseed oil used by Bailey and Baldsiefen in their mixtures had a hexabromide number of 42, while the soy-bean oil had a hexabromide number of 6. Substituting these constants in the general equation it becomes:



$$y = \frac{x - 6}{0.36} \qquad (2)$$

By substituting the determined hexabromide numbers of the prepared oil mixtures designated Samples 793 to 811 in Equation 2, the following results are obtained:

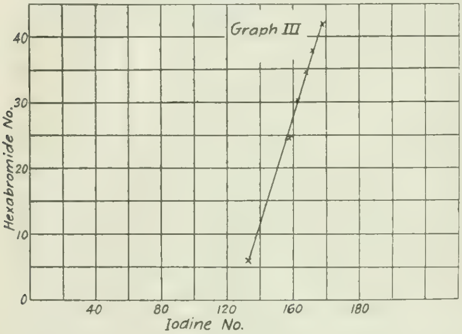
---

[1] Received April 18, 1921.

[2] This Journal, 12 (1920), 1189.

Sample No.	Hexabromide Number Detd. (1)	Hexabromide Number Corr. (2)	Linseed Oil Present Per cent	Linseed Oil Calcd. from (1) Per cent	Linseed Oil Calcd. from (2) Per cent	Percentage Difference
793	26.2	27.75	60.5	56.2	60.5	—4.3
794	33.4	33.40	76.2	76.2	76.2	0
795	39.6	39.10	91.9	93.4	91.9	+1.5
806	41.1	42.00	100.0	97.5	100.0	—2.5
807	40.7	42.00	100.0	96.4	100.0	—3.6
808	39 8	42.00	100.0	93.9	100.0	—6.1
809	35.0	33.00	75.0	80.6	75.0	+5.6
810	33.5	33.00	75.0	76.5	75.0	+1.5
811	34.8	33.00	75.0	80.0	75.0	+5.0

The corrected hexabromide numbers were obtained by substituting the per cent of linseed oil in the mixtures in Equation 2 and computing the correct values. These results show that an experimental error varying by ±1 per cent from the true per cent of hexabromides of the fatty acids present in the mixed oils produces an error differing by ±2.75 per cent from the true per cent of linseed oil in the mixture, and that the experimental error involved in the determination of the hexabromide number may lead to a deviation of ±6.0 per cent from the per cent of linseed oil actually present.



Equations 1 and 2 can be applied only to the oil mixtures used by Bailey and Baldsiefen in their work, for it is obvious that any changes in the constants will produce changes in b and m in the equations. This can be seen by reference to Graph I, where the results of Gardner's investigations[1] on the relation between the iodine numbers of linseed-soy-bean oil mixtures and the per cent of linseed oil present in the mixtures have been plotted against Bailey and Baldsiefen's results. The equation for Gardner's curve is

$$y = \frac{x - 133.0}{0.569}$$

while that for Bailey and Baldsiefen's curve is

$$y = \frac{x - 135.5}{0\ 435}$$

owing to the fact that Gardner's linseed oil had an iodine number of 189.3 and his soy-bean oil a probable value of 133.

RELATION BETWEEN IODINE AND HEXABROMIDE NUMBERS FOR ANY SPECIFIC MIXTURE OF LINSEED AND SOY-BEAN OILS

By plotting the hexabromide numbers of the fatty acids in Table III (Bailey and Baldsiefen) against the corresponding iodine numbers of the oil mixtures (Graph III), the plotted points fall on a straight line, the general equation of which is

$$y = \frac{x - b}{m} + a.$$

For this particular case, y is the hexabromide number of the fatty acids, x is the iodine number of the mixture, b is the iodine number of the pure soy-bean oil in the mixture, a the hexabromide number of the pure soy-bean oil, and m the cotangent of the angle the line makes with the x-axis. For the particular oils used by Bailey and Baldsiefen in their investigation the general equation becomes:

$$y = \frac{x - 135.5}{1.16} + 6 \qquad (3)$$

Comparing the calculated values for the hexabromide numbers of the fatty acids by substituting the corrected iodine and hexabromide numbers in Equation 3, we find:

Mixture Linseed Oil Per cent	Mixture Soy-Bean Oil Per cent	Iodine Number Determined	Iodine Number Corrected	Hexabromide Number Determined	Hexabromide Number Corrected	Hexabromide Number Calculated	Hexabromide Number Difference in Units
85	15	171.9	172.5	37.7 37.8	37.7	37.9	+0.2
75	25	168.0	168.1	34.2 33.8	34.2	34.1	—0.1
65	35	164.2	163.8	31.4 30.9	30.2	30.4	+0.2
50	50	...	157.3	23.3 24.3	24.6	24.8	+0.2

The corrected hexabromide number agrees closely with the determined values and the hexabromide number computed from the corrected iodine number by Equation 3 varies only slightly from the corrected hexabromide number.

EFFECT OF VARIATION IN THE ANALYTICAL CONSTANTS OF THE OILS

The maximum iodine number of raw linseed oil is 189.8 for oil from South American seed, while the minimum iodine number is 173.2 for oil from North American seed. For soy-bean oil the maximum iodine number is 135.5, while the minimum value is usually 127. The hexabromide number of raw linseed oil, as determined by Bailey and Baldsiefen's method, ranges from 41 to 44, while that of soy-bean oil ranges from 3.0 to 7.4. Having established the maximum and minimum constants of the pure oils, it becomes possible to estimate the error introduced into a determination by using

TABLE I

Constants of Oils in Mixture A				Per cent of Linseed Oil in Mixture A	Iodine No. of Mixture		Per cent of Linseed Oil in Mixture A Calc. from (1)	Percentage Difference	Hexabromide No. of Mixture		Per cent of Linseed Oil in Mixture A Calc. from (2)	Percentage Difference	REMARKS
Linseed Oil I No.	Linseed Oil Hex. No.	Soy-Bean Oil I No.	Soy-Bean Oil Hex. No.		Detd. B. & B.	Corr. (1)			Detd. B. & B. Av.	Corr. (2)			
189.8	44.0	127.0	3.0	85	171.9	172.5	71.7	—13.3	37.8	37.7	84.7	—0.3	Linseed
				75	168.0	168.1	65.3	— 9.7	34.0	34.2	76.2	+1.2	I No. high
				65	164.2	163.8	58.5	— 6.5	30.9	30.2	66.3	+1.3	Soy
				50	...	157.3	48.2	— 1.8	24.3	24.6	52.0	+2.0	I No. low
189.8	44.0	135.5	7.4	85	171.9	172.5	68.2	—16.8	37.8	37.7	82.8	—2.2	Linseed
				75	168.0	168.1	60.0	—15.0	34.0	34.2	72.7	—2.3	I No. high
				65	164.2	163.8	52.1	—12.9	30.9	30.2	64.3	—0.7	Soy
				50	...	157.3	40.1	— 9.9	24.3	24.6	47.0	—3.0	I No. high
173.2	41.0	127.0	3.0	85	171.9	172.5	98.6	+13.6	37.8	37.7	91.3	+6.3	Linseed
				75	168.0	168.1	88.9	+13.9	34.0	34.2	82.2	+7.2	I No. low
				65	164.2	163.8	79.7	+14.7	30.9	30.2	71.6	+6.6	Soy
				50	...	157.3	65.6	+15.6	24.3	24.6	56.8	+6.8	I No. low
173.2	41.0	135.5	7.4	85	171.9	172.5	98.3	+13.3	37.8	37.7	90.3	+5.3	Linseed
				75	168.0	168.1	86.6	+11.6	34.0	34.2	79.8	+4.8	I No. low
				65	164.2	163.8	75.1	+10.1	30.9	30.2	67.8	+2.8	Soy
				50	..	157.3	57.8	+ 7.8	24.3	24.6	51.3	+1.3	I No. high

---

[1] *Paint Mfrs. Assoc. U. S., Circular* **50** (1917)

Bailey and Baldsiefen's values for the per cent of linseed oil corresponding to a certain determined hexabromide number, when using oil mixtures containing oils having different analytical constants than those used by them in their investigation. The maximum deviations from their results will occur when the maximum or minimum values of the pure oil constants, as established, are used in the computations.

In the computations, the results of which are stated in Table I, the determined iodine and hexabromide numbers recorded in Table III by Bailey and Baldsiefen were corrected to eliminate experimental errors by the method previously described, using the following constants for their oils:

	Iodine Number	Hexabromide Number
Linseed oil	179.0	43.3
Soy-bean oil	135.5	6.0

The per cent of linseed oil corresponding to the corrected iodine or hexabromide numbers was then computed for mixtures of the two oils having the widest range of analytical constants, and the difference between the true per cent corresponding to that iodine number or hexabromide number compared with the per cent stated by Bailey and Baldsiefen to correspond to the same iodine or hexabromide number.

SUMMARY

1—The modified hexabromide method gives results differing by + 7 to — 3 per cent from the actual amount of linseed oil in mixtures of linseed and soy-bean oils containing oils having the widest range of analytical constants, when Bailey and Baldsiefen's results for mixtures of oils with average constants are used as a criterion for the determination of the per cent of linseed oil present in the mixture.

2—The experimental error of the modified hexabromide method may produce results differing by ±6 per cent from the actual amount of linseed oil in the mixture.

3—In examining mixtures of linseed and soy-bean oil containing oils, the constants of which are unknown, results differing by + 13 to — 9 per cent from the actual per cent of linseed oil in the mixture are possible under these conditions.

4—The iodine number determination gives results differing by + 16 to — 17 per cent from the actual amount of linseed oil in mixtures of linseed and soy-bean oils having the widest range of analytical constants, when Bailey and Baldsiefen's results for oils with average constants are used as a criterion for the determination of the per cent of linseed oil in the mixture.

5—The experimental error of the iodine number determination may produce results differing by ±1 per cent from the actual per cent of linseed oil in the mixture.

6—The total error involved when the iodine number of mixtures of linseed and soy-bean oil, the constants of which are unknown, is used to ascertain the per cent of linseed oil in the mixture, may lead to results differing by +17 to —18 per cent from the actual per cent of linseed oil in the mixture.

7—In all cases, for mixtures of the oils, the modified hexabromide method gives more nearly accurate results than the iodine number determination.

8—The per cent of linseed oil in mixtures of the two oils can be ascertained within ±9 per cent, using Bailey and Baldsiefen's results as a criterion, when mixtures of linseed oil with a maximum iodine number and soy-bean oil with a maximum or minimum iodine number are examined.

9—When mixtures of linseed oil and soy-bean oil with minimum constants are examined, the per cent of linseed oil as determined, using Bailey and Baldsiefen's results as a criterion, may vary from the actual amount present by 0 to + 12 per cent.

Preparation of Alcoholic Potassium Hydroxide Volumetric Solution[1]

By S. T. McCallum

Research Laboratories, McKesson & Robbins, 91 Fulton St., New York, N. Y.

A perusal of the prominent authorities on the testing of oils and fats discloses the fact that only one general method is given for the preparation of 0.5 *N* alcoholic potassium hydroxide volumetric solution. This consists in dissolving the required amount of potassium hydroxide in a small amount of water and adding a sufficient quantity of ethyl alcohol which has been especially purified by some more or less tedious method. Even when great care is used in its preparation, the solution has a tendency to darken with age and exposure to light and also to lose in strength.

For several years the author has used the following simple method for the preparation of this volumetric solution.

The correct amount of potassium hydroxide (allowing for water and carbonate) is crushed quickly in a mortar and transferred to a volumetric flask. Sufficient Columbian methanol or purified wood alcohol is added to fill the flask to the mark. The flask is then shaken occasionally till the solution is complete. The carbonate which separates out should be filtered off through glass wool. The solution is now ready for standardization.

No special purification of the Columbian methanol is required, the ordinary grade being satisfactory. A solution prepared as described above is not perceptibly darkened by exposure to light. The author has often made normal potassium hydroxide solution by this method which was practically colorless. If for any reason a water-white solution is required, all that is necessary is to distil the Columbian spirit in glass before making up the solution.

Numerous comparisons of the solution with one made by the U. S. P. method showed no perceptible variation in saponification numbers obtained on the same oil.

Association of Official Agricultural Chemists

The thirty-eighth annual convention of the Association of Official Agricultural Chemists is to be held at the Washington Hotel, Washington, D. C., October 24 to 26, 1921. The meetings will be held at the hotel headquarters.

The program includes reports of referees and special papers closely associated with the work of the Association. A special order for 11 o'clock on Tuesday, October 25, includes addresses by the president of the Association, Dr. W. F. Hand, the honorary president, Dr. Harvey W. Wiley, and by Senator E. F. Ladd. The Secretary of Agriculture will deliver an address at a special meeting in the afternoon of the same day.

Technical Association of the Pulp and Paper Industry

The Technical Association of the Pulp and Paper Industry and the American Pulp and Paper Mill Superintendents' Association are to hold their joint meeting October 18 to 21, 1921. The meeting will open in Washington, D. C., with headquarters at the New Willard Hotel. After a day devoted to the reading and discussion of papers and visits of inspection to various government bureaus, the party will leave for a trip of mill and plant inspections. Wednesday, the 19th, will be spent at York, York Haven, and Spring Grove, Pa.; Thursday, at Philadelphia, where the banquet will be held at the Bellevue-Stratford, and on Friday the members will visit plants at Wilmington, Del.

---

[1] Received May 28, 1921.

LABORATORY AND PLANT

Need of a New Table for Specific Gravity and Per cent of Glycerol[1]

By L. W. Bosart

Chemical Division, Procter & Gamble Co., Cincinnati, Ohio

Various tables have been published showing the relation of the specific gravity and per cent glycerol on purified glycerol. Of these, the tables of Gerlach, Nicol, Lenz, Strohmer, Fabian, Metz, and Skalweit may be mentioned.

In discussing the various tables, Lewkowitsch quotes Morawski as authority for the statement that "Gerlach's and Skalweit's values agree among themselves and with the results of elementary analysis."[2] For the sake of convenience, Gerlach's and Skalweit's tables from 100 to 90 per cent are here given:

Gerlach			Skalweit	
Glycerol Per cent	Sp. Gr. 15°/15° C.	Sp. Gr. 20°/20° C.	Glycerol Per cent	Sp. Gr. at 15° C.
100	1.2653	1.2620	100	1.2650
99	1.2628	1.2594	99	1.2625
98	1.2602	1.2568	98	1.2600
97	1.2577	1.2542	97	1.2575
96	1.2552	1.2516	96	1.2550
95	1.2526	1.2490	95	1.2525
94	1.2501	1.2464	94	1.2499
93	1.2476	1.2438	93	1.2473
92	1.2451	1.2412	92	1.2447
91	1.2425	1.2836	91	1.2421
90	1.2400	1.2360	90	1.2395

A. Grün and T. Wirth[3] determined the specific gravity of glycerol which had been purified by distilling twice in vacuo and drying over phosphorus pentoxide for 5 mo. They found 1.2653 ± 0.0001 at 15°/15° C. This is the figure given by Gerlach for pure glycerol, and they therefore concluded that Gerlach's table was the most trustworthy. This is undoubtedly true as far as the table for 15°/15° C.[4] is concerned, and yet certain facts must be taken into consideration that tend to show that the results are not as accurate as desirable. It must be considered that Gerlach's determinations were made by displacing glycerol with a plummet, a means which must have been very crude as compared to the pycnometer method which is now almost universally used for this work, and with which quite accurate results to the fourth decimal place are possible. His plummet displaced 86.500 g. water and 109.45 g. pure anhydrous glycerol, both at 15° C. The specific gravity of pure glycerol was therefore

$$\frac{109.45}{86.50} = 1.2653.$$

According to the figures given in Gerlach's paper[5] he made determinations on 100 per cent glycerol, 90 per cent, etc., that is, at every 10 per cent. It is significant that the digit in the fourth place is always 0 except with 100 per cent and 10 per cent glycerol, and in the latter case, the digit is 5. It is apparent that Gerlach made no attempt to figure his results closer than the third decimal except in the two cases mentioned, which was quite correct if the fourth decimal place was not significant with the method he used. For percentages between 100 and 90 per cent, between 90 and 80 per cent, etc., the specific gravity was obtained by interpolation. Here, however, he has carried his figures out to the fourth decimal place, which gives the table an appearance of accuracy which does not exist. Despite these defects, the figures appear to be fairly close to the truth.

In a communication to the writer A. C. Langmuir, who was chairman of the subcommittee on glycerol analysis of the American Chemical Society, stated that in his opinion Gerlach's table was the most accurate of those published and was nearly correct in the higher concentrations. He also stated that on a sample of glycerol elaborately purified he had obtained 1.2653 for 100 per cent and 1.2524 for 95 per cent, both at 60° F., thermometers and weights calibrated by the U. S. Bureau of Standards. 1.2653 at 60° F. would equal 1.2655 at 15° C., and 1.2524 at 60° F. would equal 1.2526 at 15° C. It will be seen, therefore, that Gerlach's table, which gives 1.2653 for 100 per cent glycerol and 1.2526 for 95 per cent glycerol at 15° C., agrees very closely with the results of Langmuir.

If, however, we consider Gerlach's table for 20° C., we find there is something very decidedly wrong. The following table shows Gerlach's figures for 100 and 95 per cent glycerol at 15° C. and 20° C., and also their values calculated for 20° C. and 25° C., assuming Gerlach's values for 15° C. to be correct and using the correction for expansion of glycerol given by Comey and Backus:[1] 0.00061 for 20° C., and 0.000615 for 25° C.

Glycerol Per cent	Gerlach		Calculated	
	15° C.	20° C.	20° C.	25° C.
100	1.2653	1.2620	1.2634	1.2617
95	1.2526	1.2490	1.2507	1.2490

The specific gravity of 95 per cent glycerol at 25° C., 1.249, given in the Pharmacopeia, agrees with the calculated value. The value 1.2490 for 95 per cent glycerol at 20° C. given by Gerlach is, therefore, obviously incorrect. The same is true of 100 per cent glycerol, for which Gerlach's value at 20° C. is quite close to the calculated value at 25° C. A number of tests made on glycerols of lower densities (from 90 to 40 per cent) agree closely with Gerlach's values at 15°, but the values for 25° were approximately those of Gerlach at 20°. It would seem fairly well established, therefore, that Gerlach's table for 20° is in reality approximately correct for 25°.

It would be a very valuable contribution to the study of glycerol if some one were to get out a new set of tables based on accurate determinations made with the best modern facilities. In September 1911, the subcommittee on glycerol analysis of the Society reported that a new specific gravity table had been prepared, using as a basis a sample of C. P. glycerol which was shown to be practically anhydrous (within a few hundredths of a per cent).[2] We do not know what has become of this table and, as far as we know, it has never been published. Certainly if it was not completed, a new one should be prepared.

Conclusions

It has been shown that the most reliable table for specific gravity and per cent glycerol is that of Gerlach at 15° C. This is sufficiently accurate, at least in the higher concen-

---

[1] Received March 14, 1921.

[2] "Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th Ed., **3**, p. 384.

[3] *Z. angew. Chem.*, **32** (1919), 59; *J. Soc. Chem. Ind.*, **38** (1919), 295*a*.

[4] Hereafter whenever the temperature is given at which a specific gravity determination has been made, it will be understood that water at the same temperature is taken as unity and the temperature given simply with one figure, as for example, 20° C. instead of 20°/20° C.

[5] *Chem. Ind.*, 1884, 277.

[1] This Journal, **2** (1910), 16.

[2] *Ibid.*, **3** (1911), 860.

trations, for practical purposes, but the fact that Gerlach did not attempt accuracy in the fourth decimal detracts from his work.

Gerlach's table for 20° C. should be discarded entirely, but it is not likely that this temperature is used to any extent, the temperatures mostly in use being 15° C., 15.5° C., 25° C., and 60° F.

New tables should be prepared for these temperatures, but until this is done the following rule can be adopted with the assurance that one will not be very far from the truth:

For 15° C. use Gerlach's table for that temperature; for 15.5° and 60° F. deduct 0.0002 from the specific gravity shown in Gerlach's table for 15° C. (for the higher percentages); and for 25° C. use Gerlach's table for 20° C.

The Sewage Testing Station of the Illinois State Water Survey Division[1]

By Edward Bartow

Department of Chemistry, State University of Iowa, Iowa City, Iowa

The Illinois State Water Survey began the study of the activated sludge process of sewage treatment in November 1914, and had progressed by stages through bottle experiments, experiments in a box 9 in. square and 4 ft. deep, comparative experiments in four tanks 3 ft. 6 in. square and 10 ft. deep, all on the fill and draw system, to experiments in the original Champaign septic tank 18 ft. by 49 ft. and 9 ft. deep, working on the continuous flow system.

Combined with the study of the process were studies of the amount of oxygen in the influent and effluent air, the bacterial flora, and the fertilizer value of the sludge formed.

The results obtained were very good, and the continuance of the work was planned, when it became necessary to discontinue it almost completely because several of the staff were called upon to enter the Army. The same conditions existed almost everywhere, and little that was new had been learned about the process by the fall of 1919, when members of the staff returned to the Division.

A small appropriation had been made for the biennium 1917–19, which was not used and had been reappropriated for the biennium 1919-21. With this as a nucleus the testing station is being revived. The Division funds have been supplemented by contributions or loans of instruments, apparatus, and machinery. The several Sanitary Districts in the State have promised their coöperation and support. Several manufacturing concerns have loaned apparatus for the work. Tanks, machinery, a blower, a filter press, a continuous filter, and a dryer have been obtained in this way.

It is not proposed to confine the experimental work to the activated sludge process, but to try other methods of sewage treatment as time and funds permit. Many cities in Illinois are located on large streams into which a partly purified sewage can be emptied. It is therefore proposed to construct and test the efficiency of methods of primary treatment, such as the Doten tanks used in the Army, the separate digestion tanks used by the Housing Corporation, and other similar schemes that may be developed.

Owing to the limited amount of funds, all of the schemes cannot be tried at once, and it has been decided to make a study first of the Dorr-Peck modification of the activated sludge process, with additions so that the process will be complete from the raw sewage to the clarified and purified effluent, and the dried sludge ready to be used as a fertilizer.

The plant is located on land belonging to the city of Champaign, near the outfall of the Champaign sewer. The site is well adapted to the purpose. Before entering the distributing chamber, formerly used in connection with the Champaign septic tank, the sewage is about on a level with the ground, and after passing the manhole the by-pass is enough lower to allow the sewage drawn from the upper level to flow by gravity through a small grit chamber, and through any screening devices that are to be tested, and then to return to the sewer.

Screening

Only one screen has been installed, used by the designers for screening tannery wastes. The water passes from the outside to the center of a revolving drum. The drum is rotated at such a rate that some of the screened liquid is carried up the inside of the drum, and flows out through the holes in the screen, thus automatically cleaning the outside surface of the screen. While it is planned to have each part of the plant large enough to treat 100,000 gallons of sewage daily, the screen will be large enough to handle 200,000 gallons, and it will be possible to test its capacity, as the branch tapped into the main sewer will carry 400,000 gallons. There are two notable advantages in the arrangement of the system:

1—The amount of sewage that can be screened is not limited by the capacity of pumps.

2—The pumps will deliver screened sewage and there will be no danger of clogging the suction pipe.

An extra drum will be provided so that, with practically no loss of time, the drums can be changed and different sizes and different arrangements of holes can be tried.

Pumping

The screened sewage passes from the interior of the drum through an opening in one end to the pump pit, from which it is delivered to the aeration compartment of the tanks by two centrifugal pumps having a combined capacity of 200,000 gallons. It is proposed to limit the flow, at least at first, to 100,000 gallons daily.

Aeration

The sewage enters the lower part of a cylindrical tank 17 ft. in diameter and 13 ft. deep. The tank is divided horizontally into two nearly equal parts by a tray, which is slightly higher in the middle than at the edges. The air is forced into the aeration chamber through filtros plates arranged in an inscribed square. Any sludge that may settle to the bottom is carried by scrapers toward the circumference. The air carries the sludge and sewage to the under side of the tray, which holds the air in suspension, as it travels toward the center to a level above that of the liquid in the tank. As the air escapes part of the liquid passes down a central downcast well into the lower compartment to be mixed again with the incoming sewage, and part passes into the upper compartment that serves as a settling chamber. Holding the air in the lower compartment below the tray has resulted in a great reduction of the amount of air required. According to tests made at Mt. Vernon, N. Y., the process will operate with one-third of the air required when it is allowed to rise directly to the surface and escape.

Sludge Separation

Part of the liquid from the upcast well passes over the outer rim, which can be raised and lowered to get the proportion desired in the settling chamber. In the settling chamber the flow of the clear liquid is toward the outer rim of the tank, where it flows into a trough or launder and runs away. The sludge is carried by revolving plows to the outside of the chamber where it drops down sludge wells to the aeration chamber to be mixed again with the sewage and air. The greater part of the purification is found to take place in the earlier stages of the aeration, so that it is proposed to run two tanks in series, using more air in the first tank, and allowing the sludge to collect in the settling tank till it flows over the rim into the trough, and then to the second tank where it receives a second treatment with a smaller amount of air. Sludge in excess is removed from the sludge wells in the second tank.

---

[1] Presented before the Division of Water, Sewage, and Sanitation at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 7 to 10, 1920.

Disposal of Effluent

The effluent from a properly operated activated sludge plant is so stable that it can be allowed to flow into the dry bed of a stream, or into a pond. It is proposed to allow the effluent from the tanks to flow into a pond formed from a former creek bed when the course of the stream was changed by the dredging of a drainage ditch. The pond will be about 30 ft. wide and 400 ft. long. During the summer an attempt will be made to grow fish in the pond. Fish have been successfully grown in sewage diluted 1:3 at Strasburg by Hofer, and at Bergedorf, near Hamburg, in the effluent from Imhoff tanks and sprinkling filters. If the experiment is successful, it will show the possibilities of improving the condition of many streams in the state, in which fish no longer exist.

Sludge Dewatering

Experiments with a small plate press and with a 12-in. centrifugal machine have already been tried. Enough has been learned to lead to the conclusion that the sludge must not be at all stale. If the dissolved oxygen disappears, the sludge gets into a condition that prevents filtration. Plans are in view to re-aerate the sludge after it is removed from the tank and thus prevent the development of anaerobic bacteria, which may be directly or indirectly the cause of filtration difficulties.

The success of the activated sludge process depends on the reduction of the cost of the air, and on the successful dewatering and drying of the sludge. Many attempts have been made, but we are not sure that any have been entirely successful. We may be repeating the work of others, but we believe with some modifications.

The centrifuge will be tried further. Most of our tests have given sludge with about 90 per cent of moisture. We hope to reduce this. A 15-plate leaf press with plates 28 in. in diameter has been ordered, and a continuous filter is already at the plant. The dewatering is only preliminary to the drying, which will be a new system.

Sludge Drying

So far as we know attempts to dry sludge have been made with the direct heat dryers. With these it is necessary to construct a large dust chamber, and a fume chamber in which the escaping gases can be washed, before they are allowed to escape from a high chimney. We are proposing to use an indirect heat dryer. The temperature at no point in the dryer rises above 205° F., and the moisture content of the sludge in several test runs has been reduced from 80 to 84 to 3 to 10 per cent without dust or unpleasant odors.

The members of the Division staff have taken a great deal of interest in the plans for the Station, and any success obtained will be due to their efforts and to the support given by the manufacturers and Sanitary Districts that are assisting in the work.

ADDRESSES AND CONTRIBUTED ARTICLES

Dyes Derived from Beta-Oxynaphthoic Acid and from J-Acid, with Reference to the Chemical Foundation Patents[1]

By A. Willard Joyce

Chemical Foundation, Inc., 81 Fulton St., New York, N. Y.

The dyes derived from β-oxynaphthoic acid and the arylamides of β-oxynaphthoic acid, chiefly the anilide known as Naphthol AS, form a very valuable class, which has received little or no attention from manufacturers of dyes in this country. The Chemical Foundation owns a number of patents which cover the processes for making some of these dyes, as well as the dyes themselves, and in some cases processes for applying the dye or its intermediates. It is the purpose of this paper to bring to your attention these patents which bear upon this particular group of colors.

The dyes derived from 2,5,7-aminonaphthol sulfonic acid, or J-acid, and J-acid derivatives will be discussed in a similar way.

Dyes Derived from β-Oxynaphthoic Acid and Its Anilides

In a recent paper by E. R. Brunskill[2] the advantages of the colors made by substituting the β-oxynaphthoic anilides for β-naphthol in the ice process were discussed.

It is well known that the colors made from the free β-oxynaphthoic acid with amines or sulfonated amines have the serious fault of washing out easily, and are not fast to rubbing. The anilides of this acid give colors which are much faster, so that the greatest development of these colors for dyeing by the ice process has been by using combinations with the anilides of β-oxynaphthoic acid, chiefly Naphthol AS or β-oxynaphthoic acid anilide.

The colors made from the free β-oxynaphthoic acid have found their greatest use as lake pigment colors. These are usually made in the form of their barium, calcium, and lead salts, which are noted for their insolubility in water and oil and for their brilliancy of shade.

The development of colors for use as lakes from β-oxynaphthoic acid or Naphthol D has been made by several of the large German dye companies, chiefly the firm of Meister, Lucius & Bruning. The first pigment color of this class which they patented was Lake Bordeaux B, Schultz Number 179. This dye is made by combining diazotized 2-naphthylamine-1-sulfonic acid (Tobias' acid), with Naphthol D.[1] As a color lake, this dye has no demand, and is not considered valuable commercially.

Another pigment belonging to this class developed by Meister, Lucius & Bruning, is Hansa Rubine, which is distinguished by its clear bluish red tint, insolubility in oil, and fastness to light. The dye used in making this pigment is made from 2,4-dinitroaniline-6-sulfonic acid and Naphthol D.[2]

The lake pigment known as Red for Lake C is made from the dye produced by combining 2-chloro-5-toluidine-4-sulfonic acid and β-naphthol. The firm of Meister, Lucius & Bruning found that by substituting Naphthol D for β-naphthol a dye was obtained possessing more valuable properties than Red for Lake C. The shade was also bluer and exceedingly pure and bright. This product is sold under the name Lithol Red 2G and 3G.[1]

---

[1] Presented before the Division of Dye Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] This Journal, 13 (1921), 309.

[1] U. S. Patent 858,065.

[2] U. S. Patent 978,865.

Other combinations of Naphthol D which have been patented by Meister, Lucius & Bruning are a bluish red pigment color from 5-nitro-2-amino-1-benzylsulfonic acid,[2] and a beautiful violet color lake made from the dye obtained by combining 1-naphthylamine-2-sulfonic acid with Naphthol D.[3]

The well-known pigment color, Lithol Rubine B or Permanent Red 4B, Sch. No. 152, is made from the dye obtained by combining *p*-toluidine-*o*-sulfonic acid with Naphthol D.[4] This was patented by the Actien Gesellschaft für Anilin Fabrikation, which has now expired. The A. G. A. F. also patented a color made from Naphthol D and 4-chloro-2-aminophenol-6-sulfonic acid,[5] which forms violet pigment lakes and is adapted for dyeing wool, after chroming, to violet shades.

A somewhat similar dye to the above was patented by the firm of K. Oehler. This is made by combining Naphthol D with 6-nitro-2-aminophenol-4-sulfonic acid.[6] This product has the valuable property of dyeing wool an indigo-blue shade and leaving cotton absolutely undyed.

Other Naphthol D colors which find use as pigment color lakes are combinations with aniline carboxylic acids,[7] such as anthranilic acid, with 2-naphthylamine-8-sulfonic acid[8] and with 2-naphthylamine-4,8-disulfonic acid.[9] These dyes are all of bluish red shade.

The process for making the anilides of β-oxynaphthoic acid is covered by a patent assigned to the Griesheim-Elektron.[10] Briefly, the process consists in treating the toluene solution of a mixture of β-oxynaphthoic acid and an arylamine, such as aniline, with a dehydrating agent, such as phosphorus trichloride.

The firm of Griesheim-Elektron, having developed and patented a process for making the arylamides of Naphthol D, naturally took the lead in developing dyes from these arylamides.

These dyes have the advantage of being adapted for use as pigment lakes, as well as for dyeing cotton by the ice process.

The following combinations have been patented by the Griesheim-Elektron: The dyes obtained by combining Naphthol AS, which is the anilide of Naphthol D, with diazo compounds of the benzene series, which contain at least one negative group, such as the chloroanilines and the nitroanilines, yield orange to Bordeaux Red shades which can be transformed into color lakes.[11]

Beautiful black to greenish blue shades may be obtained by padding cotton goods with an alkaline solution of an arylamide of Naphthol D, and then printing with a diazo solution of a diphenyl base, such as dianisidine. Beautiful greenish blue prints are obtained in this way. By using benzidine in place of dianisidine, black shades are made.[12]

By heating the arylamides of Naphthol D with formaldehyde, condensation products are formed[13] which may be coupled with a nonsulfonated diazo compound, giving red shades which can be produced separately for making color lakes, or produced on the fiber.

A beautiful bluish red of excellent fastness which is claimed to be very similar to alizarin red is produced on the cotton fiber by a combination of Naphthol AS and the nitrosoamine-alkali metal salt of *m*-nitro-*p*-toluidine.[1]

A one-bath method for printing these colors is made possible by the discovery that stable concentrated mixtures of the arylamides of Naphthol D with the nitrosoamine-alkali-metal salt can be prepared.[2]

Fast black shades are produced on the fiber by combinations of the arylamides of Naphthol D with diazo compounds of asymmetrically alkylized *p*-diamino-azo bodies, such as *p*-dimethylamino-*p*-amino-azobenzene.[3]

Dyes Derived from J-Acid and J-Acid Derivatives

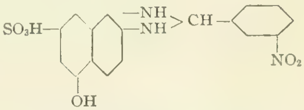
The development of new dyes from J-acid during the past twenty years has been a very important chapter in the production of new colors by the German dye firms. This class of colors is used almost exclusively on cotton, and, on account of their direct dyeing properties, combined with brilliancy of shade and fairly good fastness to light, washing, and acids, they are of special interest to the textile trade.

The development in the manufacture of direct cotton dyes in this country from the time of their first appearance upon the market to the present time can be divided into fairly well-defined groups. The first direct cotton dyes were of the Congo Red class, then came the H-acid dyes, and the Gamma-acid dyes, and at the present time we are about to enter the J-acid stage.

Foremost among the German firms in the production of J-acid dyes was the Bayer Company. The combinations patented by this company make use of the urea derivatives of J-acid, produced by the action of phosgene on J-acid, and then coupled with other arylamino compounds and amino-naphtholsulfonic acids. Other combinations were patented making use of the thiazole derivatives of J-acid, phenyl-J-acid and benzoyl-J-acid, coupled of course with other dye intermediates. The variety of shade afforded by these combinations is very great, and these colors have been put on the market as the Benzo Fast Scarlets, the Benzo Form colors, Brilliant Fast Blues, Brilliant Benzo Violets, and some of the Diazo Fast and Diazo Brilliant colors.

The German firms of Leopold Cassella & Co., Meister, Lucius & Bruning, Kalle & Co., Griesheim-Elektron, the Berlin Actien Gesellschaft, and Carl Jager have closely followed the Bayer Company in the development of the J-acid colors. It is interesting to observe the different derivatives of J-acid which each firm has specialized on in their patented products. The Cassella Company developed dyes from derivatives of J-acid known as naphthimidoazole compounds.

The compound made from amino-J-acid by condensing it with *m*-nitrobenzaldehyde has the formula:



These condensation products are now coupled with other dye components, such as arylamines and naphtholsulfonic acids or with another molecule of the naphthimidoazole compound.[4] These combinations give orange-red to scarlet-red shades which have been sold as the Diamine Fast Scarlets and Columbia Fast Scarlets.

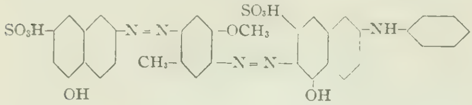
In some cases the finished dye contains free amino groups which enable the dye to be diazotized and developed with β-naphthol.[5] These colors are known as the Diamine Azo Scarlets and Oranges.

More recently Cassella patented dyes from combinations of phenyl-J-acid, amino-azo compounds and formyl-phenyl-J-acid,[6] giving violet shades. The same shades are also produced by *m*-amino-*p*-cresolmethyl ether with phenyl-J-acid.[1] An example of this class has the following formula:

---

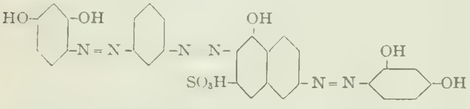
[1] U. S. Patent 983,486.
[2] U. S. Patent 1,001,458.
[3] U. S. Patent 1,016,307.
[4] U. S. Patent 741,029.
[5] U. S. Patent 1,003,266.
[6] U. S. Patent 798,808.
[7] U. S. Patent 942,916.
[8] U. S. Patent 908,580.
[9] U. S. Patent 976,401.
[10] U. S. Patent 1,101,111.
[11] U. S. Patent 1,034,853
[12] U. S. Patent 1,042,356.
[13] U. S. Patent 1.122,564.

[1] U. S. Patent 1,127,027.
[2] U. S. Patent 1,193,566.
[3] U. S. Patent 1,206,232.
[4] U. S. Patents 807,119; 813,155; 873,798; 886,985.
[5] U. S. Patents 912,182; 999,230
[6] U. S. Patent 1,020,756.



These dyes appear on the market as Diamine Fast Violet and Diamine Brilliant Violet.

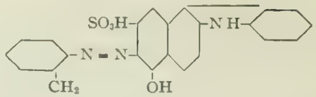
A still later development has been the production of Bordeaux Red dyes by combining *m*-amino-phenylazo-J-acid with resorcinol. These have the formula:



An after-treatment of the dyed goods with formaldehyde renders the color very fast.[2]

The dyes of this class which have been patented by Meister, Lucius & Bruning are made by combinations of benzoyl and amino-benzoyl-J-acid with arylamines and aryldiamines.[3] These dyes for the most part give yellowish red to scarlet-red shades, and are known commercially as the Diazo Brilliant Scarlets, Diazanil Scarlets, and Pinks.

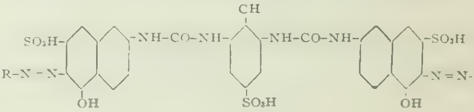
Carbazole derivatives of J-acid have been made and patented by Kalle & Co. These products are obtained by the action of phenylhydrazine on J-acid.[4] When these condensation products are coupled with diazotized arylamines, fast dyes having red to violet shades are obtained. An example of these colors has the formula:



The Naphthamine Fast Scarlets and Bordeauxs belong to this class.

Blue to violet dyes are produced by coupling dianisidine with phenyl-J-acid and another naphthol-sulfonic acid, as R-acid.[1] If metanilic acid, α-naphthylamine, 1-naphthylamine-6-sulfonic acid, J-acid and resorcinol are combined, blue shades are produced which are rendered faster by a formaldehyde treatment.[2]

The Azidine Scarlets of the Carl Jager firm are formed by the coupling of a diazotized arylamine with the urea produced by the actions of phosgene on a mixture of J-acid and 1,2,6,4-tolylenediaminesulfonic acid.[3] They have the general formula:



R = an arylamine residue.

As far as the writer is aware the production of J-acid colors is not receiving the attention in this country that it deserves; and considering the brilliancy of shade of this class of colors, combined with valuable properties as to fastness to light, washing, and acids, as compared with the older direct cotton dyes, it would seem that American manufacturers of dyes should seriously consider the immediate production of these colors.

All of the patents whose numbers are given as footnotes are the property of the Chemical Foundation, Inc.

---

[1] U. S. Patent 1,079,415.

[2] U. S. Patent 1,150,825.

[3] U. S. Patents 888,837; 941,088; 1,012,619; 1,041,146; 1,065,950.

[4] U. S. Patent 1,024,308.

[1] U. S. Patents 860,220; 860,221.

[2] U. S. Patent 1,319,852.

[3] U. S. Patent 1,006,929.

Definition of Limits for Impurities in Chemicals—Sulfate in Nitric Acid[5,6]

By W. D. Collins

U. S. Geological Survey, Washington, D. C.

A requirement frequently found in texts on the testing of chemicals is that no precipitate shall be formed when certain reagents are added. Sometimes the statement is "no weighable precipitate," sometimes merely "no precipitate," and in other tests "not more than a slight turbidity" or "opalescence." It is generally recognized that these terms are indefinite and that for many of the tests the directions are so loosely stated as to permit wide variations in the maximum quantity of the impurity which may be present without responding to the test. The requirement that the chemical pass a certain test eliminates the controversy over methods of analysis which would result from adoption of a percentage or other numerical limit for an impurity.

In an article[7] entitled "Revision of the Monographs of Official Chemicals" (of the U. S. Pharmacopeia), Arny has suggested that:

> Such tests could direct, for instance, that a 5 per cent solution of the salt mixed with definite amounts of the appropriate reagents and diluted to a definite volume, say 10 cc., should show no more turbidity than a 5 per cent solution of the C. P. chemical to which has been added a definite volume of a standard solution of the impurity plus definite amounts of the appropriate reagents and diluted to the definite 10 cc. volume, the two fluids to be compared in test tubes.

This suggestion provides for the accurate specification of concentration, so that results obtained by different analysts will be comparable and independent of individual judgment as to what constitutes turbidity or opalescence, but the requirement that the standard be a solution of a C.P. chemical to which has been added a definite quantity of the impurity makes the test impractical for many laboratories. For a chemical to be C. P. in the sense required it is not sufficient that it fail to respond to the test. It may be contaminated with a quantity of the impurity which will just escape detection and therefore give, with an added quantity of impurity, a much stronger test than should be obtained. A laboratory with none of the salt in question at hand except the sample to be examined would find difficulty in applying such a test.

Having the equivalent quantity of a pure salt in the standard test would take care of any effect on the appearance of the precipitate due to the salts in the solution. This is, however, a matter which can be worked out and stated for each test in some laboratory or laboratories where salts of exceptional purity can be prepared. If the limits for impurities are defined in terms of the precipitate formed when the reagents are added to distilled water containing a definite quantity of the impurity, the tests can be performed in any laboratory. In order that such tests may be used generally, it is worth while to sacrifice a little accuracy which might be gained by the use of elaborate or special

---

[5] Received April 19, 1921.

[6] Published by permission of the Director, United States Geological Survey.

[7] *J. Am. Pharm. Assoc.*, 9 (1920), 972.

apparatus and to require only apparatus which is in universal use.

By study of the conditions of precipitation it may be possible to select for a considerable number of tests such concentrations of acid or alkali and of reagent that the precipitation is not influenced appreciably by the presence of the salt which is being tested. The effect of impurities in reagents used in the test is eliminated by the proposed type of definition. The severity of the standard of purity can be varied by taking different quantities of the chemical to be tested and by varying the quantity of the impurity in the solution used for comparison.

Sulfate in Nitric Acid

The definition of a standard for sulfate in nitric acid will be discussed as an example of the type of definition which has been suggested.

Small quantities of sulfate are practically always estimated by the turbidity caused by barium sulfate. Conditions should be prescribed which will permit comparisons 10 or 15 min. after the addition of reagents.

Many published directions for this test indicate that the effects of different concentrations of acid and barium chloride have not been fully recognized. Directions for the determination of sulfate by turbidity given by D. D. Jackson,[1] and followed in other publications, call for 1 cc. of 1:1 hydrochloric acid and 1 g. of barium chloride crystals ($BaCl_2.2H_2O$) in 100 cc. of water. This is nearly the same as adding to a volume of 10 cc. 1 cc. of dilute hydrochloric acid (1 part strong acid diluted to 20) and 1 cc. of barium chloride solution containing 10 g. $BaCl_2.2H_2O$ in 100 cc.

Under the conditions given above it may be possible to obtain a visible precipitate with 0.01 mg. of SO_4, but the turbidity is so slight and so little more than may be found without addition of sulfate that it would not be well to recommend it as a standard limit. With 0.03 mg. of SO_4, a definite turbidity is obtained consistently. With more than 0.05 mg., the turbidity is greater than is desirable in a limiting test.

In testing nitric acid for sulfate the bulk of the sample must be evaporated before testing. To prevent loss of sulfate a small quantity of sodium carbonate or other alkali is added. For testing fairly pure acid 0.010 g. Na_2CO_3 is sufficient to hold the sulfate. As little as 0.001 g. might be used, but the results are not so consistent.

If a 20-g. sample of acid is taken it will weigh about 28 g. A limit of turbidity corresponding to 0.03 mg. of SO_4 will represent 0.000107 per cent, or for all practical purposes 0.0001 per cent. This is not an impractical standard of purity and insures good enough acid for nearly every need. If a higher purity is demanded the size of sample for test can be increased. Details of the proposed standard and test are given in the following summary.

Summary

Standards for impurities in chemicals which depend on tests which produce a precipitate should require that a definite volume of a solution of the chemical to which the prescribed quantities of reagents are added shall show no more turbidity than is produced when the same quantities of reagents are added to an equal volume of distilled water containing a definite quantity of the impurity. If possible, the quantities of reagents should be such that the presence of the salt being tested will have no appreciable influence on the result. Any unavoidable effect of this nature must be recognized in the statement of the per cent of impurity represented by the test. So far as possible the tests should require no unusual apparatus or reagents.

Reagent nitric acid should contain less than 0.0001 per cent of sulfate (SO_4) as shown by the following test:

To 20 cc. of nitric acid add 0.01 g. of sodium carbonate and evaporate to dryness. Take up in 2 or 3 cc. of water, filter, and make to a volume of 10 cc. in a test tube. Add 1 cc. of dilute hydrochloric acid (1 part of strong acid made to 20 parts) and 1 cc. of barium chloride solution (10 g. $BaCl_2.2H_2O$ in 100 cc.), and mix well. If the sodium carbonate is not known to be free from sulfate, evaporate a solution of 0.01 g. in a few cc. of water with sulfuric acid equivalent to 0.03 mg. SO_4 and 0.1 cc. of the nitric acid, and treat the residue like that from the sample. If the sodium carbonate is known to be free from sulfate the standard may be made up without it. At the end of 10 min. compare the turbidities by viewing a dark background through the depth of liquid in the tubes. The turbidity due to the sample shall not be as great as that of the standard.

---

[1] U. S. Geological Survey, *Water-Supply Paper* **151** (1905).

SOCIAL INDUSTRIAL RELATIONS

Social Research

By H. W. Jordan

Syracuse, N. Y.

CRITICISM BECOMES PLATITUDE AND OF SMALL INFLUENCE unless it be accompanied by constructive action. Through three centuries America has been a busy laboratory where earnest, conscientious men and women have experimented to attain the government and social life they believed best. Many of them, in early days all of them, came from countries of Europe where their opinions were considered destructive to the then existing order and their utterances were suppressed by imprisonment or worse. These people of vision, impelled by their convictions, transformed their criticism into action which resulted in our American republic.

They secured a far higher average of success in their pioneer experiments than we chemists or engineers do in our technical research, because they worked in close harmony with the creative action of laws of biology, which have been recognized only recently as the eternal ruling forces of social evolution. The simple social and economic development of our country, up to the opening of the epoch of complex industrial specialization, was fashioned after the biological law that those individuals or species which prove most enduring are of generalized type. Our nation was unique and substantial because the people who composed it were individually versatile and self-reliant. The whole is the sum of its parts.

THE EXTREME SPECIALIZATION that arose from intensive application of science to industry caused an abrupt departure from our distinctive American laboratory methods of social growth. The aggressive, far-sighted sort of folks who wrought our successful social experiment were drawn away, into leadership of the interesting, profitable, new pioneer domain of industrial science; America's second frontier. Our social experiment began, about 1880, to be stripped of its creative men. Their elimination was well nigh complete ten years later. Since then our government and social institutions have existed on the humus of culture that accumulated in our social soil while cultivated by the first set of American pioneers from Elder Brewster, LaSalle, William Penn and Washington to John Marshall, Lincoln, John Sherman and Phillips Brooks.

THE SITUATION HAS BECOME STEADILY WORSE in both America and England. As Alfred G. Gardiner says in the August *Atlantic Monthly*, "The transfer of power from the educated middle classes to the mass of the people, while a just and inevitable development of the democratic idea, was productive of results which were not wholly salutary. The appeal ceased to be to an instructed community, which could be reached by argument, and passed to the millions who had neither the taste nor the time for the consideration of affairs, and became interested in them only when passion was aroused."

OF THE THREE PROFESSIONS, MEDICINE ALONE, since 1880, has kept pace with industry by means of persistent, profound research. Law and church stood still, lost influence and declined in esteem. They not only devised few methods of social research, but were indifferent to science. They received little encouragement in research from static, financial powers. The recent social survey of industry, undertaken by the interchurch organization, quickly ran onto financial rocks and sunk.

Secondary education was equally impervious to science.

Hence it came to pass that few effective social measures have been originated in accordance with constructive biology. With one exception, no new order of social life has been evolved in tune with modern, specialized industry. That exception is that most of our progressive, social measures have been those of sanitation and public hygiene, in the field of the physicians. The Panama Canal was impossible until physicians and engineers tackled it under Roosevelt, the last great American pioneer. Our governmental and social practices are largely those of the early nineteenth century New England village, stretched, distorted and torn by static legislation enacted wholly without regard to biology or evolution, in well-intentioned but hopeless efforts to cover twentieth century, dynamic, metropolitan civilization.

When exploration, experiment and research stop in the chemical or physical laboratory, stagnation, mediocrity and retrogression quickly become supreme. The social laboratory reacts in like manner. The laws of social action, like those of physics and chemistry, are eternal and immutable, though but recently discovered. We can ignore them no longer.

"THERE CAN BE NO REPUBLIC WHERE THERE IS NO FRONTIER." Chemists and engineers need keep that fact ever in mind. America has explored and annexed two frontiers. The first was that of the wilderness, of the land of Plymouth Rock and Jamestown to California and back to Oklahoma. The wave of pioneer land exploration subsided into slack water with the homesteading of the last of the free land. With its subsidence, the inspiring urge of creative government and social institutions soon sank to level mediocrity. Our land pioneer epoch was that of the homesteader, the homebuilder, who was earnest and constructive in the arts of government, education and religion. Possession of land, that each settler had won from the wilderness, made those pioneers homeowning, conservative progressives. In Russia Bolshevism is subsiding, now that the peasants own the land they cultivate. In America, I. W. W. membership is recruited from the landless, homeless, unmarried, casual laborers, who have given no hostages to society.

"The rapid urbanization of the country population is a serious matter. It was the chief cause of the fall of Rome," says Dr. John J. Tigert, United States Commissioner of Education. Nobody gets excited over a rented flat, or the third floor back, unless the janitor shuts off the heat. Then we get so mad that we go to a picture show.

The rented flat, Greek restaurant, and the folding single bed loom large in OUR SECOND FRONTIER, WHICH IS THAT OF THE WILDERNESS OF SCIENCE APPLIED TO POWER DRIVEN INDUSTRY; the wilderness of contact sulfuric acid, dynamo, gasoline engine, phonograph, automobile, cinema and aeroplane. The chemists' and engineers' development of this new territory has brought maximum physical comfort, with steadily diminishing home ties and declining intellectual, spiritual idealism, upon which America was built.

OUR INDUSTRIAL FRONTIER HAS BEEN FULLY EXPLORED, standardized and brought under automatic machine, volumetric titration control by scientific research. And superpressure of the World War forced plant construction and technical education far in excess of normal requirements for some years to come. Technical schools are turning out carload-lots of chemists and engineers, many of them misguided youths whose mothers want a chemist in the family because the Gopher Prairie Gazette insists that this is a chemical engineering age. The future cannot possibly require a swelling volume of industrial research or of physical growth sufficient to employ such a steadily increasing proportion of chemists and engineers as did the past forty years.

SINCE THE WORLD WAR, WE ARE CONFRONTED BY A THIRD FRONTIER. It is the wilderness of social industrial relations, the wilderness of government, secondary education and religion, with restoration of each to its former, necessary position of creative influence. Food, clothing, housing, immigration, home ownership and full utilization of land; creative forces of world coöperative peace, rather than nationalistic forces of mutual destruction; these are subjects to which the chemist and engineer of the next two score years must apply his research. He needs to attune them with the industrial world which he brought into existence the past four decades.

How can he do this task? By the same agency through which he evolved catalytic maleic acid, gasoline engine and aeroplane. By experimentation and scientific research, by science applied to the social arts, as it has been applied to the mechanic arts. Our next article will present a practical, proven, workable plan, by which this can be done.

"The Engineers and The Price System" is the title of a recent, timely book by Thorstein Veblen. In it the author discusses nonresident, arbitrary, financial control of the great technical industries which the present generation of chemists and engineers have evolved by scientific research. "It is still the unbroken privilege of the financial management and its financial agents to hire and fire," says Veblen. "Right lately the technologists have begun to become uneasily class conscious and to reflect that they together constitute the indispensable General Staff of the industrial system. Their class consciousness has taken the immediate form of a growing sense of waste and confusion in the management of industry by the financial agents of the absentee owners. They are beginning to take stock of that all-pervading mismanagement of industry that is inseparable from its control for commercial ends. All of which brings home a realization of their own shame and of damage to the common good. So the engineers are beginning to draw together and ask themselves, WHAT ABOUT IT?"

One answer that engineers are giving is that of the Federated Engineering Council in the recent disclosures made by their Committee on the Elimination of Waste in Industry. The widespread realization of these conditions is further proved by an article—"Root, Hog, or Die," by Philip Cabot in the August *Atlantic Monthly* where, in discussing the collapse of New England railroads, he attributes their desperate condition to nonresident management and conflicting government control. Describing the spirit of their operation in the profitable days when Boston and Maine, and New Haven, sold for years far above par, Mr. Cabot says, "It was the result of a great local enterprise, owned, managed and operated by local men, on whom the responsibility for success had been squarely placed, and who had been allowed relative freedom of action." And, we may add, who were assured life-long careers as railroad men. "Current argument is largely controlled and its lines directed by the hoary tradition that the problem is a financial one, to be settled like a sum in arithmetic, notwithstanding the crop of failures which this method has produced in the past. But one is tempted to suggest that an experiment in dealing with it primarily as a human problem could not be a worse failure, and might succeed. The railroads of New England must be owned, managed, and operated by men whose homes and hearts, as well as their heads, are in New England," says Cabot.

Veblen's "Engineers and The Price System" is a frank, searching analysis of social industrial conditions, well worthy of careful reading and consideration.

"The Fruits of Victory," by Norman Angell, just published by The Century Company, should be read in conjunction with Veblen's book. Mr. Angell is a prophet whose prophecies have come true.

He calls attention to the breakdown of the transport and credit system, in Europe as in America; to the pressure of industrial city populations upon the means of subsistence, a biological pressure that is raising questions of American and world statesmanship that cannot be relieved, nor diverted to constructive work, by static, standpat, unscientific, selfish, partisan, class legislation. He cites the world general trend toward village and farm life, a movement impelled by the need to be close to food supply. "All else can be jettisoned in our complex civilization, provided only that the stomach can be filled."

The collapse of financial and governmental unscientific management brings the engineers' industrial world to the condition that, "On the one side millions are perishing for lack of corn or cotton; while on the other corn and cotton are in such abundance that they are burned, and their producers face bankruptcy."

"Much of the dense population of Europe," and we may include that of industrial America, "can only live at a standard necessary for civilization—leisure, social peace, individual freedom—by means of certain coöperative processes, which must be carried on largely across frontiers." Continuance of profitable business depends upon raising the cultural standards of the world's people; the standards, not of the few, but of the many.

HIS CONCLUSIONS ARE ALMOST IDENTICAL WITH THOSE OF Conklin, Korzybski and other social biologists, that we need devise new social economic methods, based on the law of evolution that specialization be counterbalanced by coöperation, else it destroy us; and that ancient methods of finance, diplomacy and government must give way, under biological pressure, to science applied to the social and economic arts. That the individual shall be restored to full, normal individuality, like that of the American pioneer, even though this may involve the unscrambling of some existing huge economic aggregations and their reversion, in accordance with biology, to smaller units working as in Denmark, in complete national coöperation; and that public opinion shall be founded on whole facts made clear by science, rather than on half truths muddled by a sensational press.

SCIENTIFIC SOCIETIES

Sixty-second Meeting, American Chemical Society, New York, N. Y., September 6 to 10, 1921

Program of Papers

GENERAL MEETING

John E. Teeple, Chairman New York Section. **Address of Welcome.**
Edgar F. Smith, President, American Chemical Society. **Response.**
Francis P. Garvan, President, Chemical Foundation. **Chemistry and the State.**
Sir William J. Pope. **Modern Developments in War Making.**
Professor R. F. Ruttan. **Organization of Industrial Research in Canada.**

INTERNATIONAL MEETING

Chemistry and Civilization. Dr. Edgar F. Smith, Provost Emeritus, University of Pennsylvania, in the chair.
Chas. Baskerville, Director of the Laboratories, College of the City of New York; Chairman, International Committee. **Science and Civilization: The Role of Chemistry.**
A. D. Little, Chemical Engineer and Technologist, Boston, Mass. **Energy: Its Sources and Future Possibilities.**
Leo H. Baekeland, Honorary Professor of Chemical Engineering, Columbia University. **The Engineer: Human and Superior Direction of Power.**
Sir William Pope, Professor of Chemistry, Cambridge University. **Chemistry and Life.**
Willis R. Whitney, Head of Research Department, General Electric Company. **Theories.**
C. E. K. Mees, Head of Research Department, Eastman Kodak Company. **Research Applied to the World's Work.**
Ernst Cohen, Professor of Chemistry, University of Utrecht. **Problem of Diffusion and Its Bearing on Civilization.**
W. D. Bancroft, Professor of Physical Chemistry, Cornell University. **Catalysis: The New Economic Factor.**

PUBLIC MEETING

Presentation of Priestley Portrait by C. A. Browne.
President's Address—Progress in Chemistry. Edgar F. Smith.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

C. E. Coates, *Chairman* T. J. Bryan, *Secretary*

1. Clarke E. Davis and Earl T. Oakes. **The Testing and Grading of Food Gelatins.**
2. Harrison Hale and Wm. L. Bleecker. **Chlorine as a Germicide for Milk and Milk Products.**
3. H. E. Barnard. **The Inadequacy of Analytical Data.**
4. Clarke E. Davis and D. J. Maveety. **The Chemistry of Leavening Agents.** (Lantern.)
5. N. E. Gordon. **Availability of Salts in Soils.** (Lantern.)
6. C. A. Peters and R. K. Stratford. **The Effect of Pectin, Acid and Sugar on the Character of Gels.** (Lantern.)
7. J. W. Read and Barnett Sure. **Nutritive Value of the Georgia Velvet Bean (*Stizilobium deeringanum*): Supplementary Relationship of Whole and Skimmed Milk to the Hulled Seed and the Whole Plant.** (Lantern.)
8. Barnett Sure and J. W. Read. **Nutritive Value of the Georgia Velvet Bean (*Stizilobium deeringanum*): (*a*) Supplementary Relationship of Leaf and the Hulls to Seed; (*b*) Nutritive Value of the Whole Plant.** (Lantern.)
9. J. W. Read and Barnett Sure. **Calcium Chloride as a Mineral Supplement in the Ration.** (Preliminary Report.)
10. C. E. Coates and A. F. Kidder. **Sugar Beets in Louisiana.**
11. Edward F. Kohman. **Causes of Hominy Black.**
12. L. W. Ferris. **The Volatile Acids and the Volatile Oxidizable Substances of Cream and Experimental Butter.**
13. L. W. Ferris. **Some Determinations on the Soluble Nitrogen Compounds of Cream and Butter.**
14. L. W. Ferris. **A Method for the Determination of Amino Nitrogen and Ammonia in Cream and Butter.**
15. O. L. Evenson and L. W. Ferris. **The Viscosity of Natural and Remade Milk.**
16. H. A. Noyes. **Composition Basis for Considering the Water Requirements of Plants.**

BIOLOGICAL CHEMISTRY DIVISION

Arthur W. Dox, *Chairman* Howard B. Lewis, *Secretary*

I—Symposium on Vitamines. Henry C. Sherman, *Chairman*

1. Casimir Funk. **The Antineuritic Vitamine**
2. Atherton Seidell. **Experiments on the Isolation of Crystalline Antineuritic Vitamine.**
3. A. F. Hess. **The Antiscorbutic Vitamine.**
4. R. Adams Dutcher. **Factors Influencing the Vitamine Content of Food Materials.**
5. A. D. Emmett. **Standardized Methods for the Study of Vitamines.**
6. R. R. Williams. **Vitamines from the Standpoint of Structural Chemistry.**
7. V. K. La Mer. **Vitamines from the Standpoint of Physical Chemistry.** General Discussion: Katherine Blunt, G. H. A. Clowes and Others.
8. J. S. Hughes, J. B. Fitch and H. W. Cave. **The Influence of the Vitamine Content of a Feed on the Nutritive Value of the Milk Produced.** (Lantern.)
9. R. A. Dutcher and C. W. Ackerson. **The Influence of Excessive Oxidation upon the Nutritive and Antiscorbutic Properties of Cow's Milk.** (Lantern).

10. J. S. Hughes, L. F. Payne and F. E. Fox. The Relation between the Vitamine Content of a Feed and Hatchability of the Eggs Produced.
11. L. Freedman. A Comparison of the Yeast and Bacteria Growth Promoting Vitamines.
12. B. Dass. Food Products Rich in Vitamines.
13. W. D. Richardson. The Distributor of Vitamines in Natural Foodstuffs. (Lantern.)
14. Casimir Funk and Harry Dubin. The Vitamine Requirements of Certain Yeasts and Bacteria.

II—Papers

1. F. E. Rice and A. L. Markley. Proof of the Presence of Lipase in Milk and a New Method for the Detection of the Enzyme.
2. F. E. Rice and T. Hanzawa. A Quantitative Method for the Determination of Peroxidase in Milk.
3. H. C. Sherman and Marguerite Wayman. Effect of Certain Antiseptics upon the Activity of Amylases.
4. H. C. Sherman and Florence Walker. The Influence of Certain Amino Acids upon the Enzymic Hydrolysis of Starch.
5. H. C. Sherman and Mary L. Caldwell. A Study of the Influence of Arginine, Histidine, Tryptophan and Cystine upon the Hydrolysis of Starch by Purified Pancreatic Amylase.
6. J. Bronfenbrenner and M. J. Schlesinger. Concerning the Nature of the Toxic Products of *Bacillus botulinus*.
7. H. A. Spoehr. The Internal Factor in Photosynthesis.
8. A. W. Dox, Lester Yoder and Adelia McCrea. Comparative Stability of Alkylbarbituric Acids as Determined by Availability of Nitrogen for Fungus Cultures.
9. R. E. Swain and N. W. Rakestraw. The Chemical Composition of the Body Fluids of the Sea-Lion.
10. E. T. Oakes and C. E. Davis. The Molecular Weight and Transition Point of Gelatin. (Lantern.)
11. J. S. Hepburn. The Non-Protein Nitrogen of the Hen's Egg. (Lantern.)
12. J. S. Hepburn, E. Q. St. John and Frank M. Jones. Biochemical Studies of Insectivorous Plants. (Lantern.)
13. D. B. Jones and H. C. Waterman. Studies on the Digestibility of Proteins in Vitro. III—On the Chemical Nature of the Nutritional Deficiencies of Arachin. (Lantern.)
14. D. B. Jones, A. J. Finks and C. E. F. Gersdorff. A Chemical Study of the Proteins of the Adsuki Bean, *Phaseolus angularis*. (Lantern.)
15. Howard B. Lewis and Max S. Dunn. The Hydrolysis of Casein and Deaminized Casein by Enzymes. (Lantern.)
16. C. P. Sherwin. Synthesis of Glycocoll and Glutamine in the Human Body. (Lantern.)
17. J. J. Willaman and C. A. Morrow. Revision of Rosanoff's Diagram of the Aldose Sugars. (Lantern.)
18. J. J. Willaman. The Constitution of Inulin. (Lantern.)
19. J. J. Willaman and F. R. Davison. Biochemistry of Plant Diseases. IV—Effect of the Brown Rot Fungus on Plums. (Lantern.)
20. A. A. Epstein. The Rennet Content of Pancreatic Extract and Methods for Its Isolation.
21. W. A. Perlzweig. The Immunizing Substance of the Pneumococcus. (Lantern.)
22. M. X. Sullivan. Biochemical Studies in Pellagra.
23. R. T. Balch and I. K. Phelps. A Study of the Chemical Composition of Decayed Tomatoes.
24. C. F. Langworthy and F. D. Barrett. Energy Expenditure in Sewing. (By title.)
25. C. H. Bailey and Mildred Weigley. Loss of Carbon Dioxide from Dough as an Index of Flour Strength. (By title.)
26. C. H. Bailey and Arnold Johnson. Studies on Wheat Flour Grades. III—Effect of Chlorine Bleaching upon the Electrolytic Resistance and Hydrogen-Ion Concentration of Water Extracts. (By title.)

CELLULOSE CHEMISTRY SECTION

Harold Hibbert, *Chairman* G. J. Esselen, Jr., *Secretary*

1. Walter Russell and Louis E. Wise. Acetolysis of Wood Cellulose. (Preliminary Communication.)
2. Harold Hibbert. The Constitution of Cellulose.
3. R. W. Thatcher. The Role of Cellulose in Plant Life.
4. Alfred Tingle. The Determination of the "Bromine Figure" or "Chlorine Factor" of Pulp and the Utilization of These Quantities in Bleaching.
5. Alfred Tingle. The Alleged Adsorption of Alumina from Solutions of Aluminium Sulfate by Cellulose.
6. L. F. Hawley and Subramanya Aiyar. The Distillation of Methoxyl Groups in Wood Distillation Products.
7. W. O. Mitscherling. Cellulose-di-thio-carbonic Acid Ester.
8. H. E. Wilkie. Acetic Ether as a Solvent for Nitrocellulose and Cellulose Acetate.
9. Louis E. Wise. Requirements of a Brief Critical Monograph on the Chemistry of Cellulose.
10. Report of Committee on Preparation of Standard Cellulose.
11. Report of Committee on Viscosity Standardization.

Note—It is hoped to have an informal discussion of several topics of general interest, including lignon cellulose and sulfite liquors.

CHEMICAL EDUCATION SECTION

Edgar F. Smith, *Chairman* Neil E. Gordon, *Secretary*

1. Purpose and Aims of the Section on Chemical Education.
2. David Snedden. Desirable Aims for School and College Chemistry.
3. The First Two Years of College Chemistry:
    - (*a*) William McPherson and H. N. Holmes. What General Chemistry Should Be Taught in the First Two Years?
    - (*b*) Lyman C. Newell. Parallel Courses in General Chemistry.
    - (*c*) Herbert F. Davison. Freshman Laboratory for Students Who Have Had Chemistry in High School.
    - (*d*) A. Silverman. The Systematic Care of Chemistry Students.
4. Edgar F. Smith. What Is Meant by the Spirit of Research?
5. Edward Ellery. Teaching the Elements of Research.
6. W. A. Noyes, H. P. Talbot, John C. Olsen and H. B. Dains. In What Way and to What Extent Are Departments of Chemistry Fostering the Spirit and Methods of Research? Round Table Discussion.
7. Harrison Hale. The Proper Emphasis on "American" in Teaching Chemistry.
8. Thos. B. Freas. Most Efficient Equipment for a Laboratory.
9. W. R. Whitney, M. L. Crossley, W. J. Hale, J. M. Weiss, H. D. Gibbs. Is the Average College Graduate in Chemistry Capable of Taking up Research? If Not, Why Not? Round Table Discussion.
10. Neil E. Gordon. When Will the Teaching of Chemistry Become a Science?

DYE CHEMISTRY DIVISION

A. B. Davis, *Chairman* R. Norris Shreve, *Secretary*

1. W. F. Prescott. The Dye Situation in Canada.
2. George Heyl. Contribution to the Chemistry of Cyan-Xanthen and Cyan-Acridinium.
3. J. C. Schmidt. Lakes Prepared from *p*-Phenetidine.
4. E. R. Harding. Synthesis of Anthraquinone from Phthalic Anhydride and Benzene.
5. Irwin G. Priest. A New Direct Reading Spectrophotometer for Liquids. (Lantern.)
6. H. Wales. Naphthalenesulfonic Acids. IV—The Solubilities of Some Amino Salts of Naphthalenesulfonic Acids. (Lantern.)
7. S. Palkin and M. Harris. The Preparation of α,γ-Quinolines. I—2,4-Dimethyl-6-Ethoxyquinoline: An Improved Method for Its Preparation and a Study of the Condensation. (Lantern.)
8. J. L. Bullock. Improving the Yields and Quality of Our Dyes or Reducing the Cost of Our Dyes.
9. W. A. Jacobs and M. Heidelberger. The Preparation in the Pure State of Certain Dyes of the Malachite Green Series.
10. DeWitt O. Jones. Electrometric Titration of Azo Dyes.
11. L. A. Olney. Extraction Process for Degreasing Wool.
12. Oscar R. Flynn. Fastness to Storing.
13. Warren N. Watson. Relation of Chemical Structure to Dyeing Properties.
14. Gaston DuBois. Special Cost Features and Their Relation to the Development of Our Organic Chemical Industry.
15. Leon W. Parsons and W. A. McKim. The Effect of Dye Structure on Dye Adsorption. (Lantern.)
16. J. Merritt Matthews. Is an Export Trade Necessary to the Dye Industry?
17. Joseph R. Minevitch. Preparation of Aminophenolsulfonic Acid by the Chlorobenzene Method.
18. M. L. Crossley. The Future of Research in the Dye Industry.
19. Robert E. Rose. Qualitative and Quantitative Evaluation of Dyes.
20. Francis C. Telen. A Method for the Use of Metal Sensitive Chrome Colors in Iron Machines.
21. C. R. DeLong. The Present Status of the Domestic Coal-Tar Product Industry.

FERTILIZER CHEMISTRY DIVISION

F. B. Carpenter, *Chairman* H. C. Moore, *Secretary*

I—Papers

1. Wm. H. Waggaman. Briquetting and Use of Mineral Phosphates.
2. W. S. Landis. Cyanamide in Some Fertilizer Mixtures.
3. J. E. Breckenridge. Comments on the Formation of Dicyanodiamide in Fertilizers.
4. Chas. S. Cathcart. The Value of the Alkaline Permanganate Method.
5. J. E. Breckenridge. Remarks on the Permanganate Methods for the Determination of Availability of Organic Nitrogen.
6. R. N. Brackett. Ten Years' Experience with the Neutral Permanganate Method in South Carolina.
7. Thos. C. Law. The Composition of Cottonseed.

8. H. A. Noyes, H. T. King and J. H. Martsolf. Cultivation and Nitrogen Fertilization.
9. J. J. Skinner. The Effect of Fertilizers of Various Composition on the Reaction of Soils.
10. Oswald Schreiner. The Present Tendency of Fertilizer Experimentation. (Lantern.)
11. R. Norris Shreve. Greensand as a Source of Fertilizer Potash. (Lantern.)
12. P. McG. Shuey. The Development of Accuracy in Fertilizer Analysis, and Some Pitfalls in Methods.
13. C. G. Atwater. The Determination of Free Acid in Ammonium Sulfate.
14. Paul Rudnick. On the Preparation of Hydrochloroplatinic Acid by Means of Hydrogen Peroxide.
15. H. C. Moore. Various Details in the Determination of Ammonia in Cottonseed Meal as Summarized from Eighty-six Replies to a Questionnaire Sent to Members of American Oil Chemists' Society.
16. F. P. Veitch. Wool Scouring Wastes for Fertilizer Purposes.
17. Wm. H Ross and Albert R. Merz. The Recovery of Potash as a By-Product in the Blast Furnace Industry.
18. L. S. Bushnell. A Historical Review of the Research Showing the Fertilizer Value of Sulfur. (By title.)
19. C. S. Robinson. The Preparation and Composition of Neutral Ammonium Citrate Solution. (By title.)
20. C. S. Robinson. Studies of the Availability of Organic Nitrogenous Compounds. (By title.)
21. H. A. Huston. The Potash Situation.

II—Reports of Committees

1. Fertilizer Legislation. J. E. Breckenridge, *Chairman.*
2. Research and Analytical Methods. Paul Rudnick, *Chairman.*

INDUSTRIAL AND ENGINEERING CHEMISTRY DIVISION

H. D. Batchelor, *Chairman* H. E. Howe, *Secretary*

I—Symposium on Filtration. D. R. Sperry, *Chairman*

1. Alvin Allen Campbell. Filter Cloth and Its Relation to Filtration. (Lantern.)
2. C. P. Derleth. Filter Aids. (Lantern.)
3. J. F. Springer. The Feeding of Filters. (Lantern.)
4. D. R. Sperry. Fundamental Laws of Filtration with Suggestions Regarding Research Work. (Lantern.)
5. Eustace A. Alliott. Washing and Washing Ports in Connection with "Chamber" and "Frame" Filter Presses. (Lantern.)
6. E. E. Finch. Pulp or Filter Mass Filters. (Lantern.)
7. H. D. Atkins. Atkins-Shriver Automatic Filter Press. (Lantern.)
8. H. A. Vallez. Vallez Rotary Filter. (Lantern.)
9. H. C. Beckman. Centrifugal Filters. (Lantern.)
10. Robert C. Campbell. Sweetland and Kelly Filters. (Lantern.)
11. H. A. Morrison. Oliver Continuous Filters. (Lantern.)
12. G. D. Dickey. Leaf and Rotary Suction Filters. (Lantern.)
13. Arthur Wright. Industrial Filter Media.
14. G. M. Hickey. Use of Filter-Cel for Industrial Filtration Process.
15. G. B. Rice. Plate and Frame Filter Presses.
16. D. R. Sperry. The Filter Press.

II—Symposium on the Chemistry of Gases and Fuel

C. H. Stone, *Chairman.* R. S. McBride, *Secretary*

A general discussion of chemical problems and chemical achievements in the field of gases, coking and fuels. The desirability of the establishment of a gas and fuels section of the Society will be considered if sufficient interest develops.

The following four major subjects will be discussed both by speakers arranged for in advance and by general discussion

(*a*) Coke-Oven Problems, discussion to be opened by W. H. Blauvelt, F. W. Sperr, and Others.

(*b*) Low-Temperature Carbonization of Coal, discussion to be opened by H. C. Porter.

(*c*) Gas Works Control, discussion to be opened by E. C. Uhlig, J. R. Campbell and O A. Morhous.

(*d*) Gas Analysis and Its Applications, discussion to be opened by G. W. Jones, E. R. Weaver and A. H. White.

17. Arthur L. Davis. Two New Methods for Determining Light Oil in Coke Oven Gas.
18. N. H. Gellert. Standardizing Gas Combustion by Premixing Portions of Air with Gas.
19. George G. Brown, Jr. A Chemically Controlled Automobile. (Lantern.)
20. George G. Brown, Jr. Theoretical Maximum Temperatures. (Lantern.)
21. G. W. Jones and W. L. Parker. The Formation of Oxides of Nitrogen in the Slow Combustion and Explosion Methods in Gas Analysis.
22. G. W. Jones. Present Status of Methods Used for Fuel Gas Analysis.

III -Papers

23. E. F. Collins. Electric Heat for Thermal Processes. (Lantern.)
24. Robert E. Wilson. Humidity Equilibria of Various Common Materials. (Lantern.)
25. Robert E. Wilson, William H. McAdams and M. Seltzer. The Frictional Resistance to the Flow of Viscous Liquids through Elbows.
26. W. H. Peterson and E. B. Fred. A Fermentation Process for the Production of Acetone, Alcohol, and Volatile Acids from Corncobs.
27. P. C. Haesler. A New Method of Preparing Sulfuric Acid.
28. Wilbert J. Huff. Corrosion under Oil Films and the Protective Action of Certain Colloidal Solutions.
29. Wilbert J. Huff. The Dehydration of Tar and Other Organic Emulsions.
30. C. J. Rodman. The Arc Rupture of Liquid Dielectrics.
31. H. P. Holman and T. D. Jarrell. The Effects of Waterproofing Materials upon the Tensile Strength of Cotton Yarn.
32. Special Order on World Standardization. E. C. Bingham, *Chairman.*
    The Attitude of the Manufacturer of Reagent Chemicals toward World Standardization.
    The Attitude of the Dealers in Chemicals.
    The Attitude of the University Users of Chemicals.
    The Attitude of the Technical Users of Chemicals.
    The Attitude of Great Britain and Canada toward World Standardization.
    The Attitude of the Federal Government.
    Discussion led by Charles L. Reese, W. A. Noyes, B. L. Murray, R. F. Ruttan, H. D. Hubbard, and Others.
33. W. A. Selvig and W. C. Ratliff. The Nature of Acid Mine Water from Coal Mines and the Determination of Acidity. (By title.)
34. S. H. Katz and J. J. Bloomfield. Tests of the Iodine Pentoxide Indicator for Carbon Monoxide. (By title.)
35. Mr. Stark. The Berrigan Filter. (By title.)

LEATHER CHEMISTRY SECTION

John Arthur Wilson, *Chairman* G. D. McLaughlin, *Secretary*

1. Henry Richardson Procter. Color Measurement of Vegetable Tan Liquors.
2. John Arthur Wilson and Erwin J. Kern. Color Value of a Tan Liquor as a Function of the Hydrogen-Ion Concentration.
3. Jacques Loeb Chemical and Physical Behavior of Gelatin Solutions.
4. Arthur W. Thomas and Margaret W. Kelly. The Equilibria between Tetrachrome Collagen and Liquors of Different Chrome Content.
5. Arthur W. Thomas and Margaret W. Kelly. Adsorption of the Constituents of Chrome Liquor at Various Concentrations after Nine Months' Contact.
6. Arthur W. Thomas and S. B. Foster. Influence of Sodium Sulfate, Sodium Chloride, and Sugar upon the Combination of Hide Substance with Chrome.
7. Jerome Alexander. Differentiation between Physical Mixtures and Chemical Compounds.
8. John Arthur Wilson and Erwin J. Kern. Effect of Change of Acidity upon the Rate of Diffusion of Tan Liquor into Gelatin Jelly.
9. Harold Fales. Theory and Use of Electrometric Titrations.
10. Frank L. Seymour-Jones. Chemical Constituents of Skin.
11. Alfred Seymour-Jones. The Warble Fly Problem. (Lantern.)
12. Joseph Turney Wood. The Properties and Action of Enzymes in Relation to Leather Manufacture. (Lantern.)
13. John Arthur Wilson and Guido Daub. A Critical Study of Bating. (Microscopic projection.)
14. Fini Enna. The Microscope as Applied to Leather Manufacture.
15. Arthur W. Thomas and Margaret W. Kelly. The Isoelectric Point of Collagen.
16. Alfred Seymour-Jones. Physiological and Histological Observations on the Flayed Skin Entering into the Art of Leather Manufacture.
17. William R. Atkin. The Chemistry of Lime Liquors Used in the Tannery.
18. John Arthur Wilson and Erwin J. Kern. The Determination of Tannin.
19. R. O. Phillips. Wattle Bark Tannin.
20. T. G. Greaves. Measurement of the Iron Contamination of Chestnut Extract.
21. Alfred Seymour-Jones Prophylaxis of Industrial Anthrax.
22. John Arthur Wilson. A Trip through the Tannery on the Inside of a Calfskin. (Microscopic projection.)
23. Arthur W. Thomas and S. B. Foster. On the Suspensoid Colloid Content of Vegetable Tanning Extracts with Attempts to Correlate Astringency with the Potential Difference of the Particles against the Aqueous Phase.
24. Arthur W. Thomas and Margaret W. Kelly. The Time and Concentration Factors in the Combination of Tannin with Hide Substance. I —Gambier. II Quebracho.

MEDICINAL PRODUCTS CHEMISTRY DIVISION

Charles E. Caspari, *Chairman* Edgar B. Carter, *Secretary*

1. George W. Raiziss, Joseph Gavron and M. Falkov. Arsphenamine and Neoarsphenamine. (Lantern.)
2. Paul Poetschke Hydrogen Peroxide: Its Manufacture and Preservation. (Lantern.)
3. Edwin C. White and Justina H. Hill. Developments in Mercurial Antiseptics.
4. G. D. Beal and K. E. Sparks. The Preparation of Certain Arsenic-Free Reagents.
5. G. D. Beal and J. B. Brown. The Preparation of Pure Fatty Acids.
6. G. D. Beal and J. B. Brown. The Preparation of Cholesterol Esters of Fatty Acids.
7. Francis D. Dodge. The Determination of Aldehydes in Essential Oils.
8. Michael Heidelberger and Walter A. Jacobs. Crystalline Ethyldihydrocupreine (Optochin) Base.
9. M. Dorset and J. A. Emery. The Purification of Tuberculin and the Preparation of Ophthalmic Tuberculin Discs.
10. Harvey W. Wiley. Food as a Medicine.
11. A. Richard Bliss, Jr. The Need for an Improved Formula for Fusion of Digitalis.
12. Oliver Kamm. The Toxicity of Benzyl Alcohol and Its Homologs.
13. David I. Macht. Pharmacological Examination of Normal and Secondary Propyl Alcohols.

ORGANIC CHEMISTRY DIVISION

Roger Adams, *Chairman* H. T. Clarke, *Secretary*

1. F. W. Atack. Oximes.
2. A. Lowy and R. F. Dunbrook. Organo-Tellurium Bases.
3. W. A. Noyes and W. Goebel. The Role of Acetic Acid and Ammonia as Catalysts in the Formation of Acetamide from Ammonium Acetate.
4. W. A. Noyes. Preparation of Absolute Alcohol.
5. W. A. Jacobs and M. Heidelberger. 5,8-Diaminodihydroquinine and 5,8-Diamino-6-Methoxyquinoline, and Their Conversion into the Corresponding Aminohydroxy and Dihydroxy Bases.
6. W. A. Jacobs and M. Heidelberger. The Hydrogenation of Dihydrocinchonine, Cinchonine, and Dihydroquinine.
7. M. Heidelberger and W. A. Jacobs. A New Series of Cinchona-Like Alkaloids: The Dihydroquinicinols.
8. A. Lowy and A. M. Howald. The Action of Ammonia on Chlorobenzene and Bromobenzene in the Vapor State in Presence of Catalysts.
9. C. S. Venable and E. C. Crocker. The Effect of Fuller's Earth on Pinene and Other Terpenes.
10. J. M. Bell and D. M. Carroll. A Study in Yields in Nitrating Nitrotoluenes.
11. T. B. Johnson and E. B. Brown. Studies on Nucleic Acids: The Reduction of Uracil and Cytosine by Means of Colloidal Platinum.
12. T. B. Johnson and O. Baudisch. Studies on Nucleic Acids: New Color Tests for the Pyrimidine-Thymine, Applicable in the Presence of Uracil, Cytosine and Sugars.
13. O. Baudisch. The Action of Ferrous Hydroxide-Peroxide on Thymine, Lactic Acid and Alanine.
14. W. T. Read. Synthesis of the Soporific Nirvanol (4,4-Phenyl-Ethyl-Hydantoin).
15. A. J. Hill and E. J. Fischer. The Synthesis of β-Chloroallylchloride from α, γ-Dichlorohydrin.
16. W. F. Hoffman and R. A. Gortner. The Behavior of Cystine to Acid Hydrolysis.
17. R. A. Gortner and W. F. Hoffman. A Comparison of Certain Derivatives of "Protein" Cystine and the "Isomeric" Cystine Formed by Acid Hydrolysis. (Lantern.)
18. A. W. Dox and L. Yoder. Isomeric Alkylpyridines and Color Phenomena. (Lantern.)
19. E. C. Crocker. An Octet Formula for Benzene. (Lantern.)
20. J R. Bailey, W. A. Noyes and H. L. Lochte. Diisopropylhydrazine.
21. W. L. Lewis and R. S. Bly. The Chlorination Products of Formanilide.
22. C. S. Marvel and V. L. Gould. The Preparation of Dialkyl Mercury Compounds from the Grignard Reaction.
23. A. S. Wheeler and P. R. Dawson. The Chlorination of 5-Hydroxy-1,4-Naphthoquinone. (Juglone.)
24. A. S. Wheeler and H. M. Taylor. Kelp Tar Oils.
25. R. Adams and M. F. Fogler. The Structure of Disalicylaldehyde.
26. M. S. Hoffman and E. E. Reid. Anthraquinone Thioethers.
27. W. R. Waldron and E. E. Reid. Some Derivatives from *p*-Nitrothiophenol.
28. C. E. Boord and F. F. Cope. The Reaction of Propylene, Butylene, and Amylene with Selenium Monochloride.
29. C. E. Boord, A. J. Yaney and C. W. Holl. The Use of Olefines in the Preparation of Alkyl Phenols.
30. M. L. Crossley. The Action of Sulfuric Acid on 1-Phenylnaphthalene-2,3-Thiocarboxylic Acid.
31. A. S. Richardson. Addition Compounds of γ-Pyrones and Sulfur Trioxide.
32. J. Kendall and J. J. Beaver. Compound Formation in Phenol-Cresol Mixtures.
33. W. L. Evans and P. S. Hines. The Oxidation of Potassium Acetate with Potassium Permanganate in the Presence of Potassium Hydroxide.
34. W. L. Evans and O. L. Hoover. The Oxidation of Acetol with Potassium Permanganate in the Presence of Potassium Hydroxide.
35. W. L. Evans. The Oxidation of Propyleneglycol with Potassium Permanganate in the Presence of Potassium Hydroxide.
36. Harold Hibbert and Laura G. Cannon. The Condensation of Citral with Certain Ketones and the Synthesis of Some New Ionones.
37. L. C. Raiford and J. R. Couture. The Migration of Acyl from Nitrogen to Oxygen.
38. L. C. Raiford and C. E. Greider. Acylation with α-Naphthoyl Chloride and the Migration of Acyl.
39. L. C. Raiford and H. A. Iddles. The Migration of Acyl: Effect of the Relative Positions of the Amino and Hydroxyl Groups.
40. F. C. Whitmore and B. J. Markit. Stability of Carbon-Mercury Linkage in Mercury Derivatives of Malic Acid.
41. A. J. Hill and H. R. Henze. Hydantoin Indigoids. (By title.)

PETROLEUM CHEMISTRY SECTION

T. G. Delbridge, *Chairman* W. A. Gruse, *Secretary*

I—Papers

1. C. E. Coates and B. Y. Tims. An Unusual Type of Casinghead Gasoline.
2. Thomas Midgley, Jr. Some Observations on the Polymerization of Amylene.
3. E. M. Johansen. The Iodine and Bromine Values of Petroleum Products.
4. R. E. Wilson and D. P. Barnard, 4th. Specific Heats and Heats of Vaporization of Motor Fuels. (Lantern.)
5. C. H. Osmond and T. G. Delbridge. Further Observations on the Value of the R. E. Test.

II—Symposium on Emulsification Problems in the Petroleum Industry

6. Leon W. Parsons. The Inversion of Phases in Oil-Water Emulsions. (Lantern.)
7. T. R. Briggs. Emulsions with Finely Divided Solids.
8. J. L. Sherrick. Emulsifying Agents in Oil-Field Emulsions.
9. A. W. McCoy. A Short Discussion on the Formation of Crude Oil and Water Emulsions.
10. E. E. Ayres, Jr. Common Characteristics of Crude Petroleum Emulsions.
11. R. R. Matthews and P. A. Crosby. Recovering Petroleum from Emulsions by Chemical Treatment.
12. Sidney Born. Oil-Field Practice in Handling Crude Oil Emulsions.

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

H. N. Holmes, *Chairman* S. E. Sheppard, *Secretary*

1. Harry B. Weiser. Adsorption by Precipitates. V—Adsorption during the Precipitation of Colloids by Mixtures of Electrolytes. (Lantern.)
2. Harry B. Weiser and Henry A. Nicholas. The Influence of the Concentration of Colloids on Their Precipitation by Electrolytes. (Lantern.)
3. Harry B. Weiser. Intermittent Phosphorescence. (Lantern.)
4. Arthur E. Hill. The Ternary System: Silver Perchlorate-Benzene-Water. (Lantern.)
5. Arthur E. Hill and Thomas M. Smith. Hydrated Oxalic Acid as an Analytical Standard. (Lantern.)
6. R. C. Wiley and N. E. Gordon. Effect of the History of Adsorbent on Adsorption. (Lantern.)
7. D. C. Lichtenwalner, A. L. Flenner and N. E. Gordon. Adsorption from Solution. (Lantern)
8. E. B Starkey and N. E. Gordon. Effect of Hydrogen-Ion Concentration on Adsorption. (Lantern.)
9. A. M. Baker and James W. McBain. The Sorption of Toluene and Acetic Acid and Their Mixtures by Carbon. (Lantern.)
10. Robert E. Wilson and Allen Abrams. Drop Weights of Oils in Solutions of Emulsifying Agents. (Lantern.)
11. Robert E. Wilson, William B. Ross and Leon W. Parsons. The Preparation and Properties of Ferric Hydroxide Gel. (Lantern.)
12. Robert E. Wilson and F. P. Hall. The Measurement of the Plasticity of Clays. (Lantern.)
13. Robert Herman Bogue. The Transitional Temperature of the Sol and Gel Forms in Gelatin. (Lantern.)
14. Robert Herman Bogue On the Swelling and Gelation of Gelatin. (Lantern.)
15. Eugene C. Bingham. Plasticity of Colloids. (Lantern.)
16. S. E. Sheppard, Felix A. Elliott and H. D Gideonse. The Fluidity-Pressure Curves of Gelatin Solutions. (Lantern.)

17. Geo. Shannon Forbes and H. Isabelle Cole. The Action of Dilute Chloride Solutions upon Silver Chloride. (Lantern.)
18. D. A. MacInnes and Y. L. Yeh. The Potentials at the Junctions of Chloride Solutions. (Lantern.)
19. E. T. Oakes and Henry M. Salisbury. Electrometric Titration of Orthophosphoric Acid. (Lantern.)
20. Barnett Cohen and W. Mansfield Clark. Oxidation-Reduction Potentials of Certain Indophenols and Thiazine Dyes. (Lantern.)
21. M. X. Sullivan, Barnett Cohen and W. Mansfield Clark. Oxidation-Reduction Potentials of Sulfonated Indigos. (Lantern.)
22. W. M. Clark and H. F. Zoller. A Series of Oxidation-Reduction Indicators. (Lantern.)
23. Alexander Lowry and Oswald Blackwood. Selenium Galvanometric Colorimeter. (Lantern.)
24. C. W. Foulk. A Submerged Floating Equilibrium Bob That Adjusts Its Weight to the Density of the Liquid in Which It Is Placed. (Lantern.)
25. C. W. Foulk and Samuel Morris. The Comparative Value of Different Specimens of Iodine for Use in Chemical Measurements. (Lantern.)
26. E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard. Variation of Grain Size in Photographic Emulsions in Relation to Photochemical and Photographic Properties. (Lantern.)
27. Ross Aiken Gortner and Paul Francis Sharp. The Physicochemical Properties of Strong and Weak Flours. III—Viscosity as a Measure of Hydration Capacity and the Relation of the Hydrogen-Ion Concentration to Imbibition in the Different Acids. (Lantern.)
28. Ross Aiken Gortner and Walter F. Hoffman. An Interesting Colloid Gel. (Lantern.)
29. Harold A. Fales and Harold E. Robertson. Are Electrolytes Completely Ionized at Infinite Dilution? (Lantern.)
30. W. V. Evans and R. T. Dufford. Luminescence of *p*-Bromophenyl Magnesium Bromide and Related Compounds. (Lantern.)
31. Felix A. Elliott. A Simplified Titrating Hydrogen Electrode. (Lantern.)
32. F. O. Anderegg. High Frequency Ozone Production. (Lantern.)
33. Saul Dushman. The Reaction between Tungsten and Hydrocarbon Vapors. (Lantern.)
34. Charles E. Ruby. The Activities of Ions in Mixed Electrolytes. (Lantern.)
35. H. B. Kipper. The Atomic Structure. (Lantern.)
36. Albert F. O. Germann and Marion Cleveland. The Cryoscopy of Boron Trifluoride Solutions. VI—System with Methyl Chloride. (Lantern.)
37. Alan W. C. Menzies and Sydney L. Wright, Jr. The Application of a Differential Thermometer in Ebullioscopy.
38. Claude H. Hall, Jr. The Decolorizing Action of Boneblack.
39. A. S. Richardson. Effect of Electrostatic Potential on the Activity of a Catalytic Surface.
40. C. R. McCrosky and A. J. King. The Selenides of Ammonium.
41. James Kendall and Paul M. Gross. The Correlation of Compound Formation and Ionization in Solutions.
42. James Kendall, Arthur W. Davidson and Howard Adler. The Prediction of Solubility in Polar Solutions.
43. F. P. Dunnington. The Complete Analysis of an Insoluble Silicate with a Single Fusion.
44. A. W. Bull and J. R. Adams. Alizarin-Iron Lakes.
45. A. W. Bull and J. R. Adams. Adsorption of Tannin by Gelatin.
46. V. R. Kokatnur and H. W. Stiegler. The Theory of Molecular-Compound Formation.
47. H. G. Deming and B. C. Hendricks. The Diffusion of Hydrogen through Metals. (By title.)
48. Stuart J. Bates and Alfred Stamm. The Adsorptive Property of Fuller's Earth.

RUBBER CHEMISTRY DIVISION

W. W. Evans, *Chairman* Arnold H. Smith, *Secretary*

1. Report of Committees. Executive, Physical Testing. Abstract, Chemical Analysis and Accelerator.
2. C. Olin North. Mineral Rubber.
3. Harry L. Fisher and Harold Gray. The Tetrahydroxyphenyl Derivative of Rubber and Its Tetramethyl Ether.
4. Irene C. Diner. Microscopy of Rubber Fillers. (Lantern.)
5. Benton Dales and W. W. Evans. The Use of the Microscope and Photomicrographs in the Study of Inorganic Materials Used in Rubber. (Lantern.)
6. Henry Green. Recent Developments in the Art of Rubber Microsectioning. (Lantern.)
7. G. S. Whitby and A. H. Smith. Rapid and Low Temperature Vulcanization. (Lantern.)
8. C. W. Sanderson. An Improved Oven for Accelerated Aging of Rubber. (Lantern.)
9. General Discussion. Accelerated Aging Tests. Led by W. W. Evans. Review of Article "Ten Years' Experience with Accelerated Aging Tests," by W. C. Geer and W. W. Evans.
10. J. C. Sproull and W. W. Evans. An Apparatus and Method for Abrasion Tests on Rubber Compounds.
11. W. J. Kelly. The Determination of True Free Sulfur and True Coefficient of Vulcanization in Vulcanized Rubber. II.
12. J. W. Shields. Corrected Stress-Strain Curves of Rubber.
13. W. W. Vogt. The Determination of the Particle Size of Pigments.
14. C. S. Venable and C. D. Green. The Solubility of Sulfur in Rubber.
15. C. W. Bedford and L. B. Sebrell. Reactions of Accelerators during Vulcanization. IV—Mechanism of the Action of Zinc Compounds.
16. Frederick Dannerth. The Action of Volatile Organic Solvents and Vulcanizing Agents on Organic Compounding Materials and Resinous Gums.
17. O. de Vries. The Preparation and Testing of Crude Rubber.
18. Time is here reserved for the discussion of various topics by our foreign visitors. Particular attention will be paid to the correlation of English and American ideas on chemical research and development in the rubber industry.
19. General Discussion. The Mechanism of the Vulcanization of Rubber. Remarks by C. W. Bedford, G. D. Kratz and P. I. Murrill.
20. General Discussion. Methods of Plotting Physical Testing Data. Led by W. W. Vogt.

SUGAR CHEMISTRY SECTION

C. A. Browne, *Chairman* Frederick Bates, *Secretary*

1. E. H. Adkins and J. R. Withrow. Modified Sulfate Methods for Ash in Sugar and Molasses.
2. C. E. Coates. Some Studies on Decolorizing Chars.
3. C. E. G. Porst and J. M. Kreno. The Comparison of Various Blacks upon the American Market.
4. F. W. Zerban and S. Byall. Adsorption Isotherms of Some Decolorizing Carbons. (Lantern.)
5. A. S. Elsenbast. Mechanical Clarification of Cane-Sugar Liquors.
6. H. H. Peters. Decolorizing Carbons. (Lantern.)
7. H. H. Peters. An Inquiry into Fundamentals of Sugar Colorimetry. (Lantern.)
8. F. P. Phelps. The Testing of Quartz Control Plates.
9. C. A. Browne. The Origin and Development of the Cane-Sugar Industry in America. (Lantern.)
10. H. S. Paine and F. W. Reynolds. Enzyme Method for Determining Raffinose in Sugar-House Products.
11. C. A. Browne, C. A. Gamble, G. H. Hardin and M. H. Wiley. Role of Fermentation in the Deterioration of Cane-Sugar Products.
12. C. E. G. Porst and N. V. S. Mumford. Manufacture of Chemically Pure Dextrose.
13. F. W. Reynolds. The Purification and Concentration of Enzyme Solutions for the Rapid Analysis of Sugars by Enzymotic Hydrolysis.
14. R. F. Jackson. The Estimation of Raffinose and Sucrose in Beet Products.
15. M. J. Proffitt. A Simple Diffusion Battery for Laboratory and Lecture Room Experiments.
16. H. S. Paine and C. F. Walton, Jr. Precipitation of Gum from Beet Molasses.
17. C. F. Walton, Jr., and O. S. Keener. Chemical Properties of the Beet Gum from Cane Affected by Cobb's Gumming Disease and Its Influence in the Sugar-House.
18. W. D. Horne. The Dietetic Value of Sugar.
19. C. E. G. Porst and Miss J. F. Mohring. The Organic and Inorganic Composition of Corn.
20. J. J. Willaman. Some New Processes in the Sorghum Sirup Industry.
21. C. A. Browne. Note on the First Uses of the Polariscope in the United States for Sugar Testing. (Lantern.)
22. T. S. Harding. Preparation of Fructose by Crystallization from Invert Sugar.
23. A. W. Thomas. Analyses of Mixtures of Reducing Sugars and Sucrose with Quisumbing's Fehling Solution Method.
24. C. E. G. Porst and M. Moskowitz. Use of the Plastiometer on Specifications of Corn Products.

WATER, SEWAGE AND SANITATION DIVISION

W. P. Mason, *Chairman* W. W. Skinner, *Secretary*

1. A. M. Buswell. Investigations of the Chemical Reactions in Water Purification, Using the Hydrogen Electrode.
2. W. E. Shaefer and J. W. Sale. A Study of the Wesgelszky Method for Determination of Iodide and Bromide.
3. W. W. Skinner and J. W. Sale. Purity of Bottled Mineral Waters.
4. E. M. Chamot and F. R. Georgia. Commercial Peptones and the Culture Media Used in the Examination of Water.
5. J. A. Wilson, W. R. Copeland and H. M. Heisig. A Study of the Activated Sludge Process.
6. J. W. Sale and W. W. Skinner. Mineral Composition of the Water Supply of Seventy Cities in the United States.
7. G. C. Bunker and Henry Schuber. Quantitative *vs.* Qualitative Adjustment of the Hydrogen-Ion Concentration of Culture Media.

Reports of Meetings of Divisions and Sections

DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY

The meeting of the Division was distinguished by two symposiums in addition to the general papers and a special discussion on world's standardization. The first symposium on filtration took into account all types of modern filter presses and filter media. Two papers dealing more with fundamental principles were of special interest.

Among the several excellent general papers may be mentioned that on a chemically controlled automobile which combined in instructive form the theoretical and practical phases of that problem.

The special order on World's Standardization left no doubt as to the activity of the Society's Committee on the Metric System, particularly with regard to the purchase of chemicals in standard metric packages. It is thought that with more than 150 colleges and universities purchasing in metric units some opportunity is afforded to try out the metric system.

The Division adopted a motion, to be referred to the Committee on National Policy, asking endorsement of H. R. 10, a bill to fix the metric system as the single standard of weights and measures for certain uses.

The present active committees were continued and the appointment of an assistant secretary was authorized. It was announced that the subject for the symposium at Birmingham would be on distillation and at Pittsburgh probably on cost accounting. An effort will be made in future to secure abstracts of papers to be presented at a symposium at such a time in advance as will permit preprinting and circulation to encourage discussion.

The attendance at the sessions was large and much more uniform than usual.

The following officers were elected:

Chairman: WARREN K. LEWIS.
Vice Chairman: D. R. SPERRY.
Secretary: H. E. HOWE.
Assistant Secretary: E. M. BILLINGS.
Executive Committee: W. F. HILLEBRAND, EDWARD MALLINCKRODT, JR., F. M. DE BEERS, ALEXANDER SILVERMAN, HERBERT R. MOODY, C. E. COATES.

H. E. HOWE, *Secretary*

Symposium on the Chemistry of Gases and Fuel

At the symposium on the chemistry of gases and fuels held under the leadership of C. H. Stone, chairman, and R. S. McBride, secretary, Mr. F. W. Sperr opened the discussion on coke-oven problems requiring chemical attention. He discussed particularly the need for fundamental research on coal, coke, and by-products to supplement much of the investigational work done in the past, which has been empirical. Coal research is needed particularly on the subject of the constitution of mineral fuels. In the case of coke in the past "How to make it" has been considered, but not as fully as should be the question "What is it?" The study of by-products also offers an unlimited field; for example, the utilization of cyanides, sulfocyanates, the recovery and utilization of hydrogen sulfide, and numerous light oil problems.

H. C. Porter opened the second portion of the program, the discussion of low temperature carbonization of coal. In this field the opportunity of the chemist is wholly unlimited, because as yet no commercial processes of value have been extensively applied, largely because of the limited knowledge as to the best methods and suitable application for products. The question of the characteristics of the coke to be expected from low temperature carbonization received considerable attention in discussion by a number of those present.

The discussion of needed carbonization investigations included reference to the study of the thermal history to which fuels are subjected during processing and extensive investigation needed for determination of thermochemical data. What happens inside an oven is a subject not at all well understood chemically. The possibility of greater efficiency in heat application by using the exothermic reactions which take place was also emphasized. The characteristics of coke as determining blast furnace operation is another important field receiving attention at present. The work of the Bureau of Mines on this was briefly described and the importance of it pointed out. It was made clear by Dr. Fieldner that only through a full knowledge of how coke of various types can best be used will it be possible to persuade the blast furnace operator to take any type of coke which can best be made in view of the current market requirements for by-products.

Chemistry in gas-works control was discussed by E. C. Uhlig who pointed out the large opportunity for further chemical investigation in theoretical lines which undoubtedly would afford sound basis for industrial development of the future. The distinct opportunity of the AMERICAN CHEMICAL SOCIETY in this field as distinguished from the engineering and routine method standardization work of the American Gas Association was clearly recognized. Mr. C. H. Stone, continuing this discussion, brought out clearly the numerous miscellaneous problems which are presented to the gas-works chemist for solution, including problems of boiler feed water control, tests for the purchasing department of cement hardeners, rust removers, paints, greases, lubricants, and numerous other materials, the purification of mercury for the street department, testing materials used throughout the plant, investigation of miscellaneous troubles such as deposits in mains, surface pipes, meters, and of course special problems of the regular works products.

No definite action was taken regarding an organization of a section of the SOCIETY, since the change in program date made the number in attendance so small as to prevent any general expression of opinion. Those in attendance voted to request the secretary of the Division of Industrial and Engineering Chemistry to undertake to determine whether the organization of a section would be justified and if so to formulate for the sake of those interested a request to the proper officers of the SOCIETY.

R. S. MCBRIDE, *Secretary.*

……

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

Some 200 members were present when the meeting came to order at 9:30 on Wednesday morning. All but three of the 49 papers were read. The chief interest again concentrated on adsorption, in which direction several papers of a quantitative character were presented. The papers by H. B. Weiser showed that the accepted theories of the influence of the electrolyte in precipitation of suspension colloids would have to be revised. Several papers were presented on solvated colloids and an interesting discussion of the transition from the sol to the gel form arose, Bingham's criterion of plastic flow being utilized.

Other notable features were papers by W. M. Clark and collaborators on oxidation and reduction potentials and a description by R. A. Gortner of an interesting gel formed by dibenzoylacetone.

At the business meeting the subject of chief importance was a discussion of ways and means for continuing and extending a journal of physical chemistry. Drs. E. C. Bingham and A. W. C. Menzies proposed that this question be brought before the meeting, and Drs. H. N. Holmes and J. W. McBain supported the motion with instances of the importance of maintaining such a journal. In view of the probability that Professor Bancroft's existing *Journal of Physical Chemistry* would stop by January 1, 1922, after a period of 25 years, it was felt that immediate action was desirable. After various suggestions with regard to financing an editorial board of control, it was moved and carried that a committee be appointed by the chairman to report to the meeting as to a definite proposal for forming a permanent representative committee of physical chemists of the English speaking world to consider the question and report to the SOCIETY. The chairman appointed the following committee: E. C. Bingham, G. A. Abbott, S. Dushman, A. W. C. Menzies, and J. Kendall to consult with J. W. McBain, representing the British visitors. At the same time the following motion was carried:

> The Division views with great regret the probability of discontinuance of the *Journal of Physical Chemistry* and the consequent lessening of the opportunities of physical chemists to publish the results of their work. It requests Professor Bancroft to assist for one more year the development of physical chemistry in this country by continuing the publication of the *Journal.* It recommends that as many members as possible give their support both by contributing papers and by subscribing to the *Journal.*

The committee recommended the appointment of a representative committee to consider the future policy of the physical chemists of America toward the *Journal* and the probability of enlarging its scope by coöperation with the physical chemists of the British Empire. It was proposed and carried that the nomination of this representative committee be in the hands of a committee consisting of the president and secretary of the SOCIETY for the forthcoming year and three others. It was announced by Dr. Menzies that Professor Bancroft agreed to continue the *Journal of Physical Chemistry* for one year, during which time it was hoped that the proposed international journal could be brought into being.

A special executive committee meeting recommended to the Division that in future abstracts of papers must be mailed to the Secretary of the Division by the last day of receipt of papers, thus conforming with the practice of other sections. This proposal was put to the meeting and passed.

Election of officers took place and the following were elected:

Chairman: S. E. SHEPPARD.

Secretary: R. E. WILSON.

Executive Committee: WILLIAM BLUM, JOEL HILDEBRAND, J. H MATHEWS, L. C. NEWELL, H. B. WEISER, E. C. BINGHAM, G. S. FORBES.

S. E. SHEPPARD, *Secretary*

. . . .

DIVISION OF SUGAR CHEMISTRY

This meeting, the fourth since the Sugar Section was organized, was opened with the announcement from the chair that the full privileges of a division had been granted, which announcement was enthusiastically received.

The meeting was notable for its large attendance, many branches of the science and industry represented, and for the number, variety, and quality of the papers read.

The joint committee appointed by the Sugar Section and the Division of Agricultural and Food Chemistry at the Rochester Meeting to establish new and more accurate tables for refractometric work on sugar solutions reported progress and promised to give a final report at the meeting to be held next spring at Birmingham, Alabama. The retiring chairman, Dr. C. A. Browne, who had guided the Section from its beginning through to its organization as a Division was tendered a rising vote of thanks for his untiring and devoted efforts in building up the Section.

The notable feature of the meeting was a highly interesting lecture by C. A. Browne illustrated by lantern slides as well as by a number of fine old prints tracing the history of cane sugar manufacture from the earliest time to the beginning of the industry in America and its further development in this hemisphere to modern times. The same speaker presented another note of historical interest showing pictures of two of the earliest saccharimeters used in the United States. Unusual interest was manifested in a number of papers on decolorizing carbons, a subject of great importance to all branches of the sugar industry at the present time.

It was pointed out by H. H. Peters that the methods for the determination of the color of sugar products devised decades ago are entirely inadequate for solving the modern problems of decolorization and that the entire subject must be investigated, involving highly technical studies of a fundamental character. Rapid progress is being made in these investigations and it is confidently expected that the problem will soon be solved satisfactorily.

C. E. Coates reported on a method for the preparation of decolorizing char from sugarcane bagasse, and C. E. G. Porst and J. M. Krno gave data on the decolorizing power on glucose solutions of various carbons partly purchased in the market and partly prepared by themselves. F. W. Zerban and S. Byall presented lantern slides of logarithmic adsorption isotherms, depicting the adsorption of coloring matter by various carbons from cane molasses solutions of various concentrations. There were several animated discussions in connection with these papers on decolorizing carbons which plainly showed that this entire subject is still in its formative stage and that it will require the combined efforts of representatives of a number of different sciences to coördinate and systematize the results obtained by individual workers.

There were also a number of valuable and interesting papers pointing out new and improved methods of analytical procedure for sugar work and on fundamentals underlying these methods. The determination of raffinose was dealt with by H. S. Paine and F. W. Reynolds as well as by R. F. Jackson; the estimation of reducing sugars and sucrose by A. W. Thomas; the determination of ash by E. H. Adkins and J. R. Withrow; the preparation and properties of the gums in beet molasses and in diseased sugar cane by H. S. Paine, C. F. Walton, Jr., and O. S. Keener; the use of the plastiometer on corn products by C. E. G. Porst and M. Moskowitz; and the testing of quartz control plates by F. P. Phelps.

Other papers dealt with new apparatus and new methods for the preparation or manufacture of certain sugars and sirups. W. D. Horne in an interesting contribution on the dietetic value of sugar pointed out that at present prices cane sugar is the cheapest foodstuff on the basis of calorific value, with the one exception of oatmeal.

The following officers were elected for the coming year:

Chairman: S. J. OSBORN.

Vice Chairman: F. W. ZERBAN.

Secretary-Treasurer: F. J. BATES.

Executive Committee: C. A. BROWNE, C. E. COATES, W. D. HORNE, W. B. NEWKIRK, H. S. PAINE, H. E. ZITKOWSKI.

F. J. BATES, *Secretary*

DIVISION OF FERTILIZER CHEMISTRY

The meeting of the Fertilizer Division was called to order Wednesday afternoon and continued and completed Thursday morning. A register of the names of those attending numbered forty-two.

Some of the former meetings of this Division have been more largely attended than was this one. However, one of the most interesting programs ever presented was enjoyed, as was plainly manifested by the lively discussion which followed the presentation of the papers.

A number of interesting papers were presented by the chemists representing the U. S. Department of Agriculture, showing the results of their efforts to conserve and utilize various waste materials, such as low-grade phosphate rock, wool scouring waste, and potash in blast-furnace gases. Other papers showed the results of fertilization experiments and the effect of various fertilizers both on the soils and on the crops grown.

Several papers were presented dealing mainly with analytical methods.

An interesting paper was presented showing the effect of fertilizer experiments on vineyards and the marked effect of organic matter in the soil and the cultivation of the soils to permit aeration.

Two papers were presented with reference to potash for fertilizers; one showing the relative resources of the United States, France, and Germany, and the other describing a method for extracting potash from greensand and illustrating a plant now under construction for this purpose.

Two papers discussed cyanamide and its mixture and reaction in mixed fertilizers. These were an answer to the claims of Harger (paper presented at the Chicago Meeting of this Division) that cyanamide when mixed with acid phosphate is converted into dicyanodiamide, which is toxic to plants. Neither of the authors of the two papers mentioned have been able to confirm Harger's results and in some mixtures where dicyanodiamide was deliberately added it could not be found, indicating it had been quickly converted into other complex forms. Considerable discussion followed these two papers.

Four papers considered the application of the permanganate methods for determining the availability of organic nitrogen in fertilizers and fertilizer materials. Some of the weaknesses as well as the advantages of the methods were referred to. It was pointed out that it is just neither to the fertilizer manufacturer nor to the farmer to base the reports of the fertilizer control officials relative to the quality of the organic nitrogen in the fertilizers on the availability of the water-insoluble organic nitrogen alone, but it should instead be based on the availability of the total organic nitrogen. Considerable discussion followed the reading of these four papers.

The same officers were elected to serve for the ensuing year.

H. C. MOORE, *Secretary*

. . . .

DIVISION OF RUBBER CHEMISTRY

The general trend of discussion in the Rubber Division was along the line of improving plantation rubber, the nature of vulcanization, improving the wear of tires, and increasing the aging qualities.

Dr. de Vries (17), coming from the Central Rubber Plantations in Java, gave us considerable data on the preparation and testing of plantation rubber and asked coöperative research between the plantation men and factory chemists.

The Analytical Committee had not been able to arrive at a standard method of analysis.

The Accelerator Committee reported the analysis of about 40 trade-name accelerators.

The Physical Testing Committee reported tentative methods for testing the degree of vulcanization and proper cure of a rubber compound.

There was much sentiment expressed for coöperation in research between the different manufacturers and also between the manufacturers and producers. As a result a resolution was addressed to the Rubber Association as follows:

> It is a recognized fact that there are certain fundamental principles of general interest to the rubber industry as a whole which no single company should be expected to .. develop.
>
> Therefore it is the sense of the Rubber Division of the AMERICAN CHEMICAL SOCIETY, numbering approximately 200 members from all the leading companies, both large and small, .. that a coöperative research laboratory be established under the auspices of the Rubber Association of America for furthering the investigation of such fundamental problems.

It was the largest and most interesting meeting of the Rubber Division ever held, approximately 150 attending the full two days' sessions, which would have lasted longer had there been time. Though the entire program was given with the exception of "The Action of Volatile Organic Solvents and Vulcanizing Agents on Organic Compounding Materials and Resinous Gums," by Frederick Dannerth, the discussions had to be sharply limited to complete in time.

Officers for the following year were elected as follows:

Chairman: C. W. Bedford.
Vice Chairman: H. E Simmons.
Secretary: A. H. Smith.
Executive Committee: W. B. Wiegand, W. W. Evans, J. B. Tuttle, D. F. Cranor, F. G. Breyer.

A. H. Smith, *Secretary*

……

DIVISION OF LEATHER CHEMISTRY

The Leather Division undoubtedly offered the greatest program dealing with the fundamental chemistry of leather manufacture ever presented anywhere. The leading leather chemists of Europe contributed in no small way to the success of the program, as admirably represented by Frank L. Seymour-Jones of Wrexham, Wales (who will remain to do research work at Columbia). Procter, Wood, Seymour-Jones, Atkin, and Enna are all well known on this side of the Atlantic and their contributions were received with deep appreciation. Mr. Alfred Seymour-Jones sent a large collection of photomicrographs to be presented to the proposed American Tanning School, which will in the meantime be kept at the Leather Research Department at Columbia University. The Secretary was directed by the Division to send a cable of felicitations to the International Association of Leather Trades' Chemists, meeting in London at this time, because of the contributions of their leading members to our program.

It was a disappointment to the members that Dr. Jacques Loeb was unable to attend the meeting because of serious illness in the family and hence did not deliver his paper on "Chemical and Physical Behavior of Gelatin Solutions."

The keynote of the meeting was coöperation upon the fundamental chemistry which is common to leather chemistry, and biological and other industrial fields. The majority of papers contributed to the development of fundamental principles of the chemistry of leather manufacture. Of especial importance in this connection, besides those given by the European chemists, were those by Thomas, Foster and Kelly and by Wilson, Kern and Daub.

There was an unusually large and appreciative attendance and the spirit of the meeting proved that the development of chemistry in the leather industry is now well under way. While the Leather Division is still in its infancy it has seemed to the best interest to hold one meeting a year, and it was voted to hold the next meeting with the Society at the Pittsburgh Meeting next September.

The officers elected for the coming year are:

Chairman: J. A. Wilson.
Vice Chairman: J. S. Rogers.
Recording Secretary: A. W. Thomas.
Executive Committee: Frank L. Seymour-Jones, R. McKee.

John Arthur Wilson, *Chairman*

……

DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY

All papers on the printed program of the Agricultural and Food Chemistry Division were delivered, with the exception of the paper by Edward F. Kolman, entitled "Causes of Hominy Black."

The following officers were elected:

Chairman: T. J. Bryan.
Secretary: Clement Starr Brinton, U. S. Food Inspection Station, 134 S. 2nd St., Philadelphia Pa.

T. J. Bryan, *Secretary*

……

DIVISION OF BIOLOGICAL CHEMISTRY

The most interesting feature of the meetings of the Division of Biological Chemistry was the Symposium on Vitamines under the chairmanship of Professor Henry C. Sherman. This symposium, which was held on Thursday morning and continued on Friday, was featured by unusually interesting papers and discussions by Funk, Dutcher, LaMer, Williams, Seidell, Emmett, and Hess. Particular attention was called to the necessity for a proper standardization of methods for vitamine study in order that it might be possible to secure a repetition of experiments of one laboratory in another laboratory under careful control conditions. This discussion continued throughout the meetings informally. In consequence of this interest in standardization, at the business meeting held on Friday a committee was appointed under the chairmanship of Dr. A. D. Emmett of Detroit, to make a study and recommendations for the standardization of the methods for vitamine study. This committee was instructed to coöperate as far as might be with the American Society of Biological Chemists, the Society of Experimental Biology and Medicine, and the Committee on Food and Nutrition of the National Research Council. The other members of the committee are as follows: Alfred Hess, New York; E. V. McCollum, Johns Hopkins; L. B. Mendel, Yale; and H. C. Sherman, Columbia.

At the annual business meeting the following officers were elected:

Chairman: H. B. Lewis, University of Illinois.
Secretary: J. S. Hughes, Kansas Agricultural College.
Executive Committee: R. D. Swain, Leland Stanford; R. A. Dutcher, Penn State College; H C Sherman, Columbia University; H F. Zoller, Detroit; A. D. Emmett, Detroit.

H. B. Lewis, *Secretary*

……

DIVISION OF ORGANIC CHEMISTRY

This Division held a satisfactory and enthusiastic session; of 41 papers in the program 35 were read. As is usual the greater number of the papers dealt with subjects which, while of scientific interest to the assembled specialists, are not of a nature to appeal to the general public. Two papers from the laboratory of Professor T. B. Johnson of Yale are likely to be of general interest in their application, being connected with the chemistry of the tubercle bacillus. A paper by E. C. Crocker of Massachusetts Institute of Technology, dealing with an octet formula for benzene, is the first of what it is hoped will be a long series of contributions to organic chemistry stimulated by the theories of G. N. Lewis and A. C. Langmuir.

The following officers were elected for the coming year:

Chairman: H. T. Clarke.
Vice Chairman-Secretary: F. C. Whitmore.

H. T. Clarke, *Secretary*

……

DIVISION OF CHEMISTRY OF MEDICINAL PRODUCTS

In the absence of the Chairman and Secretary, Dr. E. H. Volwiler was elected temporary chairman and Dr. Michael Heidelberger temporary secretary.

The committee appointed at the Rochester Meeting, of which Dr. Fischelis was chairman, to make recommendations concerning the correlation of manufacture of medicinal products with clinical testing, reported that progress had been made, but that additional time was needed to complete the work.

Papers were presented by G. W. Raiziss on arsenicals, and by E. C. White on mercurials. Dr. G. D. Beal reported some work on the preparation of various fatty acids and their esters, and M. Heidelberger on Optochin. In addition to several other papers reported, a number were left over until the next meeting.

The following officers were elected for the coming year:

Chairman: Edgar B. Carter.
Secretary: E. H. Volwiler.
Executive Committee: A. D. Hirschfelder, Charles E. Caspari.

E. H. Volwiler, *Acting Chairman*

……

DIVISION OF DYE CHEMISTRY

The most successful meeting of the Dye Division yet held embraced the reading and discussion of 20 papers on the use, application, and manufacture of dyes and intermediates. Particularly interesting on account of its bearing on the conditions and future development of the industry was a paper by Dr. Gaston DuBois in which he gave a well-prepared discussion of depreciation, obsolescence and general burden charges, calling the chemists' attention to these important considerations and pointing out that they should not be left solely for the attention of cost accountants.

Timely papers were contributed by the Color Investigation Laboratory of Washington, by The Rockefeller Institute of Medical Research, and by numerous other sources.

Officers elected for the ensuing year were:

Chairman: W. J. Hale.
Vice Chairman: L. A. Olney.
Secretary-Treasurer: R. Norris Shreve.
Executive Committee: B. A. Ludwig, R. E. Rose.

R. Norris Shreve, *Secretary*

DIVISION OF WATER, SEWAGE AND SANITATION

The program of the Division of Water, Sewage and Sanitation was presented in full. All of the papers were of unusual interest, eliciting an unusual amount of discussion. Papers by A. M. Buswell and R. E. Greenfield entitled "Investigations of the Chemical Reactions in Water Purification. Using the Hydrogen Electrode," the paper by E. M. Chamot entitled: "Commercial Peptones and the Culture Media Used in the Examination of Water," and the paper by G. C. Bunker and Henry Schuber on "Quantitative *vs.* Qualitative Adjustment of the Hydrogen-Ion Concentration of Culture Media" were especially well received, and lively discussion followed the presentation of each. The suggestions contained in the paper of G. C. Bunker recording the reaction of culture media has a very definite bearing on the significance of biological results in judging the purity of water supplies. The paper by W. W. Skinner and J. W. Sale entitled "Purity of Bottled Mineral Waters" recounted the activities of the Bureau of Chemistry in the inspection of commercial bottled waters during the period of ten years. The paper on the activated sludge process which is being studied by J. A. Wilson, W. R. Copeland and H. M. Heisig to determine the practicability of the installation of the method at Milwaukee was the subject of considerable discussion and comment.

Officers of the Division elected for the year 1922 are as follows:

Chairman: A. M. BUSWELL.

Vice Chairman: F. R. GEORGIA.

Secretary-Treasurer: W. W. SKINNER.

Executive Committee: W. R. COPELAND, Milwaukee Sewage Commission; W. D. COLLINS, U. S. Geological Survey.

W. W. SKINNER, *Secretary*

……

SECTION OF PETROLEUM CHEMISTRY

The Petroleum Section, which was organized at Rochester in the spring, met in sessions extending over three days. The attendance and the close interest and attention given the papers and discussions showed that the Section is filling a need felt by members interested in both the practical and the theoretical sides of the subject of petroleum chemistry.

On Wednesday afternoon a discussion was held with regard to the policy the Section should adopt in stimulating the interest of university chemists engaged in research on practical chemistry both physical and organic, in the many and absorbing problems, offered by the various phases of the petroleum industry. It was brought out clearly that progress could be made only by research done under conditions which would permit the investigator to forget economic considerations and to concentrate upon the underlying theories of the broad fields of physics and chemistry involved. This can best be done in universities, and means were discussed for bringing about the desired closer association and coöperation. It was pointed out that much theoretical work on petroleum chemistry so far published has been done by Russians, and as the unfortunate conditions in that country make further contributions from that source unlikely for many years, the duty of the United States to take up this burden becomes clear. In this connection Dr. Van H. Manning, Director of Research for the American Petroleum Institute, gave an interesting account of the work being performed along the lines of discussion, pointing out the close agreement between the desires of the members of the Section and the research objects of the American Petroleum Institute.

The program consisted of a general portion including papers on a wide range of subjects and a symposium on emulsification problems in the petroleum industry. In the first section a paper by E. M. Johansen on "Iodine and Bromine Values of Petroleum Products" suggested interesting speculations on the real composition of petroleum and its heavier fractions, while R. E. Wilson's paper on "Total Heats of Motor Fuels" supplied data of value to the automotive engineer.

The Symposium on Emulsification in Crude Oils brought together a number of keenly interested persons and prompted stimulating discussion. Oil emulsions were considered theoretically by L. W. Parsons and by T. R. Briggs; the general characteristics of petroleum emulsions by E. E. Ayres, Jr.; emulsifying agents in oil fuel emulsions by J. L. Sherrick; while the practical resolution of crude oil emulsions was presented by R. R. Matthews and P. A. Crosby, and by Sidney Born. In discussion H. C. Eddy and F. W. Lane gave interesting details of electrical processes.

Before adjournment the Section voted that the articles included in the symposium be published together, if possible. The Section also voted to petition the Council for change of their organization to that of a Division as soon as possible.

W. A. GRUSE, *Secretary*

SECTION OF CELLULOSE CHEMISTRY

The New York Meeting was the fourth consecutive meeting at which a special time and place has been set apart for the consideration of the chemistry of cellulose. The first two were symposiums under the auspices of the Industrial Division and the others regular meetings of the Cellulose Section. The interest at the present session was well sustained and the discussions free and valuable. There seemed to be general appreciation of the fact that in view of the very considerable amount of work on cellulose chemistry which is being done abroad we in this country will have to put special emphasis on this important field if our many cellulose industries are not to be left woefully behind in the race.

In an interesting paper Dr. Hibbert, chairman of the Section, outlined the results which have appeared since the last meeting bearing on the constitution of cellulose. Dr. Hawley of the Forest Products Laboratory told of some of the research of that institution which has considerably increased the yield of methanol in wood distillation. The paper by Dr. Tingle on the "Alleged Adsorption of Alumina from Solutions of Aluminium Sulfate by Cellulose" aroused much discussion, both among paper men and manufacturers of aluminium sulfate.

Professor Hibbert presented the report for the Committee on the Preparation of Standard Cellulose. At the recommendation of the committee it was voted that Dr. Johnsen be requested to present for publication a proposed method for the preparation of the standard sample of cellulose and that a copy be sent by the Secretary to each member of the Section with the request that criticisms be sent direct to Dr. Johnsen, c/o Hammermill Paper Company, Erie, Pa.

The report of the Committee on Viscosity Standards was presented by Dr. Esselen, chairman of the Committee. By means of a questionnaire sent to the manufacturers and users of cellulose ester solutions the Committee had found that the number of laboratories using the falling ball method for determining viscosities was in large majority. They therefore recommended that they be authorized to proceed to draw up a set of standard conditions for carrying out this method. A vote of the Section authorized that this be done.

The paper by Professor L. E. Wise on the "Requirements of a Brief Critical Monograph on the Chemistry of Cellulose" excited much discussion. It was finally voted that a copy of the paper be sent to Dr. John Johnston and that he be advised that it was the opinion of the Section that a textbook on cellulose should be first prepared, to be followed later by monographs on specialized phases of the subject.

The Section voted to petition the proper authorities to form the Section into a Division.

The same officers were recommended for reappointment for another term.

G. J. ESSELEN, JR., *Secretary*

……

SECTION OF CHEMICAL EDUCATION

The meeting was opened by Dr. Edgar F. Smith, chairman of the Section. He briefly discussed its purposes and aims. In part, he said that teachers should have a place to compare notes and that the purpose of the Section of Chemical Education was to furnish such a forum. "A section on chemical education is just as important as a section on any division of science. I think in the end it will create greater unity in our teaching and lead to an improvement in the teaching of chemists."

Professor David Snedden of Teachers College, Columbia University, gave a paper on "Desirable Aims for School and College Chemistry." He advanced the thought that there should be two courses of chemistry. The first type should be essentially cultural and the second prevocational. "The first should culminate in varied appreciations, the second in definite powers of execution or performance. The first should not involve as 'hard' pedagogy as the second."

"What General Chemistry Should Be Taught in the First Two Years of College" was discussed by William McPherson and Harry N. Holmes. The courses differed somewhat as to order and detail, but each outline was of high merit.

Lyman C. Newell's paper on "Parallel Courses in General Chemistry" gave a detailed plan of the proper division of freshman classes. In brief he expressed the opinion that parallel courses in general chemistry can be given profitably if certain conditions are fulfilled. Division into classes should be based mainly on entrance credit or non-credit in chemistry. The textbooks used must differ fundamentally in treatment but not essentially in scope. Methods of instruction in the non-credit class should follow traditional lines, though advantage may well be taken of every opportunity to incorporate facts, principles and theories needed in advanced courses. In the credit class, the instruction should provide an occasional opportunity to review the descriptive parts of general chemistry from a college standpoint but more especially a continuous opportunity to discuss and apply the modern interpretation of chemical change. Laboratory work should differ particularly in the manipulation needed and the interpretation demanded.

In the discussion which followed it was evident that the parallel courses were quite widely approved.

Herbert F. Davison contributed to the parallel course idea by giving in some detail the line of work used at Brown University for students who had had chemistry in high schools. The list of experiments which he gave were of a physical chemistry nature, and included a great deal of quantitative work. He believed in giving detailed directions.

A. Silverman gave a paper on "The Systematic Care of Chemistry Students," in which he brought out many details which are overlooked or neglected by the average teacher.

A symposium was given on "The Spirit of Research" by Professors Smith, Ellery, Noyes, Talbot, Olsen, and Dains. Time was the only thing lacking in making this of the highest importance and interest to all present. Dr. Ellery gave an outline for teaching the elements of research as it is being tried out at Union College. His discussion showed that he had given this matter much thought. His experiment is worth careful study, and one that will be watched with a great deal of interest. Dr. Noyes emphasized the importance of a thorough and broad foundation for those who are to take up research. He favored the chemistry major carrying out a piece of research in his senior year. This had a double purpose: first, to teach him how to find out what has been done on a problem by looking up literature, and second, to interest him in contributing to the field of chemistry. The main goal is to get the student to like the work, but at the same time he must realize that his promotion will depend largely on what he can produce.

Dr. Talbot spoke briefly of the two possible kinds of research, the highly organized research and the less organized research. He said that each had its advantage. He emphasized the fact that the instruction in chemistry must be such that the student will realize that the subject is not a finished product, and that he wished to have a hand in extending the field. He pointed out the fact that instructors must be given some leisure time in which to do research, if the spirit of research is to be fostered in the department; but he said this means expense, and it is overhead expense that is holding up a great deal of excellent research to-day. He said that the research work must not be measured by credit hours. The undergraduate idea of credit is being carried over too much into the graduate work. The graduate work must be something that contributes to science regardless of time credit.

Dr. Olsen said that the first requisite for the spirit of research was to get the proper attitude of mind in the student. He believes that the spirit of research can be and should be taught early in chemistry education. Definite and nonflexible courses tend to kill the spirit of research. The student might better do less, and do well what he does. He thinks more emphasis should be put on original work which is of the student's own choice.

Dr. Dains pointed out the importance of the teacher's making it plain to the student that all chemical knowledge is the product of man's work and that the student has a very good chance in having a part in its future development. He believes that the spirit of research is contagious and hence the necessity of research being carried on in a department simultaneously with the teaching of chemistry. He clearly pointed out that all men are not capable of research.

Dr. Harrison Hale pointed the different ways in which teachers might emphasize "America" in teaching chemistry. He said that this emphasis could best be kept in mind by becoming interested in (1) American chemical history and achievement, (2) magnitude of American resources, (3) fundamental importance of chemistry to America, and (4) American responsibility and opportunity.

Dr. Freas pointed out in a most interesting way that students need good equipment if good results are to be expected. Dr. Freas discussed specific equipment of the building, such as ventilation, plumbing, steam, compressed air, light, hot plates, and hot water, etc. Time proved too short to give the audience as much information as they desired.

"Is the average college graduate in chemistry capable of taking up research? If not, why not?" This question was one that enlisted the keen interest of both commercial chemists and teachers of chemistry. After the subject had been formally opened by M. L. Crossley, J. M. Weiss, H. D. Gibbs, and Dr. Rose in a most interesting and clear way, many extremely helpful suggestions were added by various members of the Section. The general conclusions seem to be that some college graduates were not capable of research and never would be because they did not have the scientific viewpoint while other college graduates failed because they lacked a thorough preparation in the fundamentals.

Some universities, for example, Johns Hopkins and Pittsburgh, are subjecting the college graduate to an examination before he is allowed to proceed with work leading to a doctor's degree.

"When Will the Teaching of Chemistry Become a Science?" was briefly discussed by N. E. Gordon. He tried to point out certain situations and conditions that would modify the original tendencies of the student in such a way as to make them energizing elements in chemical education.

The chairman, Dr. Smith, asked the pleasure of the Section in regard to formal organization. A motion was made and seconded that the Section be formally organized by a committee appointed by the chairman. An affirmative vote was unanimous.

NEIL E. GORDON, *Secretary*

The Effect of Chemical Reagents in the Microstructure of Wood—Correction

In the article by Allen Abrams appearing in the September issue of THIS JOURNAL under the above title, the following corrections are to be made in the material appearing on pages 788 and 789:

The cuts of Figs. 1 and 3 are transposed; also the cuts of Figs. 4 and 6. Fig. 6 is upside down.

The magnifications should read as follows: Figs. 1 to 3, × 75; Fig. 4, × 475; Figs. 5 to 10, × 160; Fig. 11, × 90, and Fig. 12, × 475.

The Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese—Correction

In the footnote on page 764 of the September issue of THIS JOURNAL the name of Dr. C. G. Fink was incorrectly printed as C. J. Fink.

Calendar of Meetings

Technical Association of the Pulp and Paper Industry—Fall Meeting, Washington, D. C., Philadelphia, Spring Grove, York, York Haven, Pa., and Wilmington, Del., October 18 to 21, 1921.

Association of Official Agricultural Chemists—Thirty-eighth Annual Meeting, Washington, D. C., October 24 to 26, 1921.

American Institute of Chemical Engineers—Annual Winter Meeting, Baltimore, Md., December 6 to 9, 1921.

The Board of Scientific Advice, Bangalore, India, has had under discussion the question of starting a sulfuric acid factory in connection with the iron works at Bhadravati, at the request of the government, with a view of developing an industry which will permit economic utilization of the by-products. The manufacture of tanning extracts, of lac, and the development of the sugar industry are also being investigated. It is planned to send students to the West Indies to learn the manufacture of sugar on a really scientific basis. It is also believed that there is a field for the manufacture of drugs, and if possible a careful investigation of medicinal plants available in the country and a study of the Ayurvedic and Unani pharmacopeias will be made during the coming year, preparatory to the development of this industry.

The journals of Singapore and Hong Kong have announced the discovery of a new rubber shrub, called octotilla, which grows wild widespread over very large areas. A very appreciable amount of rubber can be obtained from this source and at the present time the factories are extracting about one ton of crude rubber a day from this plant. The ton of crude rubber will yield about 200 lbs. of gum.

The University of Iowa is to have a new chemistry building which when completed will cost $1,000,000. About $400,000 of the $500,000 appropriated for building purposes by the last general assembly are to be used for the erection of the first units of this building.

WASHINGTON LETTER

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

With Congress on vacation, legislative Washington is nearly at a standstill. The Finance Committee of the Senate, of which Senator Penrose is chairman, has announced little progress on the tariff and tax bills, the two most important measures before Congress, which have been intrusted to the mercy of this committee.

THE TARIFF BILL

The fate of the dye embargo is still unknown. The tariff bill, although its hearings were ended with last month, has been laid aside while the tax bill is being considered, and it seems probable that tariff will not again receive attention until the tax bill is disposed of. The latest move in tariff matters has been an effort to secure a return to the tariff policy of free raw materials, and while it is not expected that the finance committee will recommend the return of mineral raw products and semicrude materials to the free list, it is expected that the duties will be cut down in many cases. What will be the effect of the recent resolutions adopted at the great meeting of chemists last week in aiding the cause of the American coal-tar industry cannot be foretold.

The dye control bill that continued the licensing system of the emergency tariff act was passed and signed by the President just before the adjournment. There was no real opposition to this measure although it afforded an opportunity for considerable discussion on the embargo plan incorporated in the permanent tariff act.

THE TAX BILL

A bitter fight over the tax bill is predicted by those who have followed the proposals of tax revision. Secretary of the Treasury Mellon has recommended continuation of the excess taxes on cosmetics, perfumes, toilet preparations, proprietary articles and patent medicines, but he suggests the transfer of the burden from the retailer to the producer and importer. This is planned in order to make up for the loss due to the proposed repeal of the excess profits tax, the capital stock tax, and the income surtax.

THE DISARMAMENT CONFERENCE

Washington is looking forward to the Disarmament Conference, which will bring many thousands of foreigners and visitors to the city. Plans for this important event and the program that will be considered are not yet known, and it is too early even to guess whether the American delegates to the conference will give serious consideration to the "broad question of our chemical industry as affected by the development and the maintenance of the chemical industry in the several nations," as they were requested in resolutions adopted by the AMERICAN CHEMICAL SOCIETY at the New York Meeting.

THE UNEMPLOYMENT CONFERENCE

Another conference, which is intended to result in the bringing together of labor, business and the Government to find out just what is the remedy for the unemployment situation that confronts the country, is to be held in Washington within the next two weeks. This unemployment conference, called by President Harding and managed by Mr. Hoover's Department of Commerce, will be attended by representatives of the chemical and dye industries among those from other key industries. A long list of names has been submitted to the President from which it is understood that selections will be made, omitting so far as practicable duplication of industries and sections. These names were suggested by the National Chamber of Commerce, the American Federation of Labor, and other representative sources. Membership at the conference will be limited to fifty or less. Data for use at the conference is being gathered by the Department of Labor.

HEARINGS ON THE METRIC SYSTEM

Those who favor the use of the metric system of weights and measures in trade in this country will have a chance to urge this system at hearings to be conducted by a subcommittee of the Senate Committee on Manufactures. Senator McNary of Oregon is chairman of the subcommittee and the other members are Senators Weller and Jones of New Mexico. The bill to be considered will be that introduced by Senator Ladd, and preliminary hearings are planned as soon as Congress returns from its recess. From the interest shown in the world standardization conference at the New York Meeting and the fact that chemists are in the habit of thinking metrically, it is expected that there will be many chemists on the pro-metric side of the question.

GRADUATE STUDY FOR GOVERNMENT EMPLOYEES

In two departments of the Government the scientific worker has a chance to do more than his regular work in the way of improving his scientific training. Both the Bureau of Standards and the Department of Agriculture are offering, this fall, courses of graduate study that can be taken by their technical employees. This is not an innovation at the Bureau of Standards, where advanced courses in physics, mathematics and chemistry have been given after working hours for more than ten years, but this is the first time that the Department of Agriculture has offered courses of graduate study. The Bureau of Standards courses include: Advanced optics, differential equations, chemical thermodynamics, and interpretation of data. Among the Department of Agriculture courses are: Biological chemistry, plant pathology, statistical methods, genetics, agricultural economics, physics of the air, mathematical statistics, economic entomology, soil physics, agricultural economics, plant genetics, plant physiology, animal genetics and plant cytology. Such courses of study, given after office hours, enrich the student and enhance the value of the service he renders to the Government.

It is expected that the administration will shortly announce the conclusions of the Joint Committee on Reorganization. Tentative reports will probably be made the basis of special legislation to authorize the merger of various agencies and this will give authority to take the necessary steps to harmonize government work in every line. Unofficial announcements indicate that a Department of Public Works and a Department of Public Welfare will be established, that the Department of Labor will be abolished, and that the Army and Navy will be combined under a Department of National Defense.

No decision has yet been arrived at by the governmental authorities on the Muscle Shoals Nitrate Plant offer. Mr. Ford was recently invited to Washington by the Secretary of War to discuss the terms of his offer. It has been reported that another offer for the project will be made by southern capitalists who have successfully promoted water power projects in the South. The offer of the Birmingham interests will probably receive further attention. Opposition has developed to the Ford offer and is being expressed through the Merchants' Association of New York, on the ground that the Government would suffer a total loss of $164,000,000 during the one-hundred-year lease.

Dr. E. D. Ball, Assistant Secretary of Agriculture, has resigned, effective October 1, but he will remain at the department as director of scientific work. Dr. Ball in this capacity will have even greater opportunities to inaugurate such beneficial schemes as the educational plan, for which he is largely responsible.

The appointment of the permanent chief of the Bureau of Chemistry has been delayed because of the impossibility of finding a properly qualified chemist who is willing to take the position at the $5000 salary attached to it. As a result of this situation, an increase in appropriation to $7500 will be asked, but under present conditions no Congressional action is likely before the middle of next year.

The bulletin of the Bureau of Foreign and Domestic Commerce of the Department of Commerce, "Commerce Reports," has been changed from a daily to a weekly publication. The change was made in order to allow a grouping of the trade information and an analysis of the data gathered for the benefit of the business and technical men of the country. New divisions, covering the large basic industries, have been formed in the Bureau and the men who have been placed in charge are recognized experts in their lines. The regional divisions of the world have been redivided from a geographical standpoint so that division chiefs can specialize and be of maximum service. A new division of commercial law has been created which will pay special attention to commercial codes.

P. L. Palmerton has been named chief of the newly established rubber division of the Bureau of Foreign and Domestic Commerce, and Arthur B. Butman of Boston has been made chief of the new division of shoes, leather, and hides.

September 15, 1921

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

In my July letter I gave you some information about the Alsatian potash industry and since that time much has developed here in France about the management of the mines. Almost daily the French papers publish some article on the subject which arouses public opinion.

In 1919 German manufacturers declared that they did not fear the competition of Alsatian potash because of the fact that the Alsatian mines had only a very rudimentary industrial and commercial organization.

Since the armistice the administration of the potash mines has been entrusted to Mr. Helmer, a lawyer at the Colmar bar, elected senator in 1920. Under his direction the extraction of potash, which was 350,000 tons in 1913, rapidly reached 1,060,000 in 1920. The profits have increased in like proportion. The general crisis, which made itself felt at the beginning of 1921, made necessary a reduction of the production by about one-third, and the financial condition of the enterprise has necessitated assistance from the banks. The management of the sequestration administrator is being criticized.

Just at present the situation is especially strained because another Alsatian manufacturer, Mr. Koch, is entering an action to establish the ownership of stock bought by him immediately after the armistice, which according to his opponents he owns only as a representative of German interests. If this were so, the Germans would possess an important part in the ownership of Alsatian potash. Actions are at present entered under different jurisdictions.

But aside from these conflicts between people and interests, there is indeed only a difference in conception of the best method of development. The development of all mines within the hands of a single company would alone make it possible to struggle commercially against German competition. Further, the single development would be preferable from the technical point of view. This argument is opposed by the advocates of a development entrusted to different companies, who could combine for purposes of export sale.

The unitary system of development would have the disadvantage even from the technical point of view of entrusting too heavy work to a single management. It would be better for a technical competition to be felt among the engineers of different companies. Moreover the unitary development would lead gradually to potash becoming a state monopoly in some form or other, and in a country so agricultural as France it is preferable that competition remain. Whatever may be the result of all these discussions, it must not be thought, as was emphasized in the journals a month ago, that part of the Alsatian potash mines are going to become German again. When Parliament convenes again at the beginning of November, judgments will be rendered and a decision will be reached.

The Disarmament Conference and the Chemical Industries

The question of disarmament which is being considered at Geneva by the League of Nations and which will be treated at the conference in Washington, which we owe to the happy initiative of President Harding, could not be completely studied without considering that the chemical industry is an arm of war of the same rank as cannon or the aeroplane.

Mr. Walter Berry, president of the American Chamber of Commerce in Paris, has given great publicity to the idea which is already widespread among chemists, but to which the public has not yet paid enough attention, that the chemical industry, and especially the dye industry, can very easily be changed almost instantly for the manufacture of war gases. All the allied countries, which since the war have created or perfected their dye industries, have had this plan in mind. Germany, forced to disarmament, has developed her chemical industry more and more toward this end. It is a common saying that the war of the future, if unhappily there must be another, will be a chemical war. It is not useless to recall that, in September and October 1918, sixty per cent of the shells used were gas shells. It is very evident that the gases used then have had their day, and that the protective apparatus which corresponded to them would be equally useless now. Very prudently, the industrial and official laboratories are working on new gases and new masks.

This is why the conference at Washington will do useful work if it succeeds in establishing the relation of the ordinary chemical industry with that of the manufacturer of toxic war products.

Progress in the Cement Industry

Numerous harbor investigations, both with a view to their equipment and to the utilization of the energy of the tides, have caused research for cements which would be resistant to sea-water, and also reasonably cheap.

Important progress has been made in this field by perfecting the manufacture of fused cement. This product, which was studied in 1908, is obtained by fusion of silica, alumina, oxide of iron, and lime. This is being manufactured now in Savoie in the Alps by fusion in the electric furnace.

Motor Fuels

I have already mentioned to you the competition which is being conducted on the use of alcohol mixed with gasoline in explosion motors. This competition will close January 1, 1922. The first prize amounts to 300,000 francs.

The trend of opinion would seem to demand that this competition give to alcohol a greater part than was originally intended. If this competition has, as an end, to favor French agriculture, considered as a producer of alcohol, it seems that it would be necessary to lower the quantity of hydrocarbon in the mixture, since we are still obliged to import the hydrocarbon. There is even the possibility of studying not the alcohol-hydrocarbon mixture burned in a gasoline engine, but a motor which would use alcohol exclusively. This latter solution will in all probability be the subject of competition next year, but the present competition is limited to the alcohol-gasoline mixture.

Although from the industrial point of view it seems premature, it is necessary to announce the discovery by Mr. Mailhe of a process which makes possible the production of hydrocarbon which may be used in motors, by the combustion of vegetable oil vapors, especially linseed, in the presence of catalysts. These vapors are first directed over copper mixed with magnesia heated to 450°. Under these conditions a liquid is collected whose vapors are passed over reduced nickel. A mixture of hydrocarbons is finally obtained.

A meeting of the Société de Chimie Industrielle is to take place in Paris, October 9 to 12. Messrs. Matignon and Claude will discuss nitrogen, and Mr. Gall, cyanamide. There will also be visits to factories. Furthermore, profiting by the example of the United States, we are attempting an exposition of chemical industries. At the start it is difficult to include all industries. The exposition has, therefore, been limited to two classes, the equipment of laboratories and the dye industry.

September 12, 1921

In the free instruction offered by the City of New York through its Evening School System for the season of 1921–1922 is a course in industrial chemistry which is given at the Stuyvesant Evening Trade School, the Bushwick Evening Trade School, the Brooklyn Evening Technical and Trade School, and the Long Island City Evening High and Trade School. Courses are open to those now employed in some branch of the industry and the instruction given is supplementary to day-time occupations, the aim being to fit the individual for greater earning capacity.

The Bureau of Standards standard sample of lead-base bearing metal No. 53 is now being issued with a provisional certificate. This sample has the approximate percentage composition: lead 79, tin 11, and antimony 10, and contains in addition small amounts of bismuth, copper, iron, and arsenic. The price of this sample is $2.00 per 150 g., prepaid or parcel post C. O. D.

Renewal No. 33*a* of Nickel Steel No. 33 is also ready for distribution at the price of $2.50 per 150 g.

There is much interest among the instructors at the University of Texas in reports of a find of potash deposits in Crane County, the western portion of the State. Mr. D. D. Christian, field geologist of the University's Bureau of Economic Energy, has completed a survey of several counties, including Crane County, and has tested some of the exposed salts in Crane County, and believes from the samples that he has found the greatest deposit of potash in the world. Mr. Christian believes that in the sections of Crane County which he examined, and near which the Atlas well is now drilling, potash will be found at about 1500 ft., and the strata will be from 100 to 200 ft. in thickness, which would make it a greater find than any of the deposits in Germany or Alsace, the chief sources of supply for the world.

INDUSTRIAL NOTES

The new plant of the Portland Vegetable Oil Mill Co., Portland, Ore., will be ready for operation in October. The plant represents an outlay of $1,000,000 and is expected to develop into an important industry.

The American Tar Products Company has begun work on its $1,500,000 Chicago plant. The company is to build a pipe line from the By-Products Coke Company for tar transportation and other residue, after Chicago's gas is made from coal.

A request has been made for assistance in developing insulating material to suit the special requirements of the British Air Ministry. Great strides were made during the war by British manufacturers in this line, but evidently the subject is by no means exhausted, and much remains to be done.

The following table, compiled from reports made by producers to the United States Geological Survey, Department of the Interior, shows the quantity, value and average selling price of lithopone marketed in the United States in 1919 and 1920:

	Quantity Short Tons	Value	Average Selling Price
1919	78,465	$10,218,850	$130.40
1920	89,373	12,484,925	139.69
Increase	11,098	2,266,075	9.29
Percentage	14.0	22.2	7.1

The figures for 1919 previously published by the Survey represented lithopone manufactured, not lithopone marketed.

The New York market quotations for lithopone showed very little variation throughout 1920, the lowest price being 7.25 cents per pound and the highest 8.5 cents. The price quoted at the close of the year was 8 cents; the average quotation for the entire year was 7.9 cents.

The Interstate Commerce Commission has granted to the railroads permission to lower the freight rate on imported vegetable oils for shipment from Pacific coast ports to the Atlantic seaboard so as to meet competition for such freight which now exists as a result of the lower rates named by steamship lines operating direct by way of the Panama canal. The new rate, which went into effect on August 1, is $1.05 per 100 lbs., as against $1.20, the former rate. A movement is on foot to have the rate reduced to 75 cents per 100 lbs., which may be acted upon shortly.

The Vicose Company of America has purchased from the Charleston Industrial Corporation fifty-two acres at Nitro, W. Va., in the center of the powder city. Three large pulp mills are included in the purchase. Pulp is to be manufactured at the Nitro mills from cotton linters for the manufacture of artificial silk in the company's plant at Chester, Pa.

An absorption plant is being erected on the Dingman No. 1 well near Okotoke, in Alberta, for the purpose of absorbing gasoline from wet gas, which is blowing out of the well at the rate of between two and three million feet daily. The gas at this well is so heavily laden that when the tap is taken off the minute globules of oil form a bluish gray column projecting several inches above the mouth of the opening.

Rogers, Brown & Company have been appointed sole agents in the United States for the sale of Virgin Aluminum, of various grades, produced by the Norsk Aluminum Company of Christiania, Norway. Stocks of aluminium will be carried at New York City and Cleveland, Ohio.

The Service Bureau of the American Wood Preservers' Association has just been established with headquarters in Chicago. It is hoped that this Bureau will be of direct benefit to all users of wood, lumbermen, engineers, farmers, the wood preservation industry, and all interested in the conservation of our forest resources.

The plant of the United Indigo and Chemical Company at Chelsea, Mass., has been seriously damaged by a fire which followed an explosion of chemicals. The loss is placed in the vicinity of $125,000.

As a result of experiments in Melbourne in the production of the bases for dyes from coal tar and its by-products, the firm of Australian Dyes Proprietary, Ltd., has been established, and a small factory will soon be in operation. The concern will be an entirely Australian business, carried on with Australian capital, labor and plant. It is expected that within twelve months the output will be 150 tons a year and that in two years the whole of Australia's requirements will be manufactured. So far a range of absolutely fast colors, including fifty-four different shades, has been proved, and this number is being increased All types of dyes are to be produced—acid, basic, chrome, alizarin, nigrosin, and many others.

PERSONAL NOTES

Dr. Arno Behr, Perkin Medalist and charter member of the American Chemical Society, died at his home in South Pasadena, Cal., on June 26, in his seventy-fifth year. While engaged at first in sugar refining, his most conspicuous achievements were gained in the glucose industry, most of the manufacturing processes employed therein having originated with him. Dr. Behr retired from active work in 1900. A full record of his brilliant work may be found in the *Journal of the Society of Chemical Industry*, April 15, 1909.

Mr. Frank N. Smalley, forty-five, chief chemist for the Southern Cotton Oil Co., Savannah, Ga., manufacturers of paint, cotton-oil products, etc., died August 14, in Boston, while on vacation. Mr. Smalley was with the Southern Cotton Oil Co. for 18 years, and was prominent in national chemical and other scientific circles. He was a graduate of Massachusetts Institute of Technology.

Miss Emma Francis resigned as head of the nutrition laboratory, Battle Creek Sanitarium, Battle Creek, Mich., last July and has been appointed assistant professor of chemical agriculture in the Experiment Station of Pennsylvania State College, beginning September 15.

Mr. E. F. Hickson, until recently associate engineer in the department of technical control, American Writing Paper Co., Holyoke, Mass., has been reinstated at the Bureau of Standards as associate chemist, under Mr. P. H. Walker.

Mr. George W. Corrie has accepted the position of assistant instructor in chemistry at Pratt Institute for the coming year.

Mr. C. E. Mangels resigned as chemist in charge of the Commercial Dehydration Laboratory, Bureau of Chemistry, U. S. Department of Agriculture, to accept a position as cereal chemist at the North Dakota Agricultural Experiment Station, Agricultural College, N. D. Mr. Mangels assumed his new duties the latter part of last July.

Dr. Dwight C. Bardwell has left Berkeley, Cal., where he received his Ph.D. at the University of California, to accept a position as assistant physical chemist at the Rare and Precious Metals Station of the U. S. Bureau of Mines located at Reno, Nevada. Dr. Bardwell will work under Dr. S. C. Lind on research problems presented by the radium at this station.

Mr. Edmund C. Champion, connected for the last nine years with the American Agricultural Chemical Company as division superintendent, and assistant manager of its four works in the vicinity of New York, has left that firm to enter the industrial engineering field as a consultant, specializing in the fertilizer and portland cement industries. Mr. Champion will continue to reside at Elizabeth, N. J.

Director Bain of the Bureau of Mines has appointed a board of engineers, consisting of Mr. M. H. Roberts, Dr. R. C. Tolman, and Prof. W. L. DeBaufre, to study the production of helium at the Petrolia, Texas, plant.

Mr. Cesare Protto has recently been appointed assistant director of the Sales Division of the Dyestuffs Department of E. I. du Pont de Nemours & Company in place of Mr. E. V. Patterson who has resigned.

Mr. Glenn E. Matthews has accepted a position as research chemist in the photographic department of the Eastman Kodak Co., Rochester, N. Y.

Mr. G. Ross Robertson has completed his graduate study at the University of Chicago and has accepted an instructorship in the Southern Branch of the University of California, at Los Angeles. While in Chicago Mr. Robertson also assisted Dr. Stieglitz in his Public Health Service work, as junior chemist, which position is now held by **Mr. Arthur P. Locke,** who recently resigned from the faculty of Morningside College, Sioux City, Ia., and who is at the same time completing his work for the doctorate.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

PRESIDENT OF THE UNITED STATES

Naval Petroleum Reserves. Executive Order committing administration and conservation of all oil and gas-bearing lands in naval petroleum reserve No. 3 in Wyoming, and naval shale reserves in Colorado and Utah to the Secretary of the Interior subject to supervision of the President, but directing that no general policy as to drilling or reserving lands located in naval reserve shall be changed or adopted except upon consultation and in coöperation with Secretary or Acting Secretary of the Navy. No. 3474. 1 p. 1921.

WAR DEPARTMENT

Preliminary Report on Investigation of Methods for Preventing Corrosion of Metal Parts of Airplanes. Material Section Report 121. 4 pp. 1921. Air Service Information Circular, Aviation Vol 3, No. 211.

TARIFF COMMISSION

Tariff Information Surveys. Revised edition, 1921. First edition was issued by Ways and Means Committee.

F-L-18. On articles in paragraphs 501–503 of Tariff Act of 1913 and related articles in other paragraphs. **Sulfur and pyrites, fulminates and explosives.** 50 pp Paper 5 cents.

Census of Dyes and Coal-Tar Chemicals 1920. Tariff Information Series No. 23. 118 pp. Paper, 10 cents. 1921. This report is a survey of the domestic dye and coal-tar chemical industry in 1920. It presents the results of a special investigation as to the production of dyes and coal-tar chemicals in the United States and of the imports of dyes. The report is divided into four parts as follows: I—A summary of developments in dyes and coal-tar chemicals, 1920; II—the production of dyes and coal-tar chemicals in 1920; III—dyes imported for consumption in the United States, 1920, calendar year; and IV—an appendix.

PUBLIC HEALTH SERVICE

Factors Governing the Selection and Protection of Sources of Water Supply. J. K. Hoskins. Supplement No. 39 to the Public Health Reports. 20 pp. Paper, 5 cents. 1921. The following factors are considered: the nature and extent of use of the contemplated supply; the sources available; the quantity of water available; the quality of available supplies; the possibilities of pollution of the supply; the natural safeguards that may be employed for protecting the supply; and the cost of installation and operation of the system.

Quantitative Pathological Studies with Arsenic Compounds. C. W. Hooper, A. C. Kolls and K. D. Wright. Hygienic Laboratory Bulletin 128. 84 pp. Paper, 15 cents. 1921.

Disinfectant Testing by the Hygienic Laboratory Method. Public Health Reports, **36,** 1559–64. A method is described in detail for determining the phenol coefficient of disinfectants which supersedes the methods given in previous publications of the Public Health Service and is the present Hygienic Laboratory method.

GEOLOGICAL SURVEY

Asphalt and Related Bitumens in 1919. K. W. Cottrell. Separate from Mineral Resources of the United States, 1919, Part II. 19 pp. Published July 18, 1921. The quantity of native asphalt and related bitumens produced and sold in the United States in 1919 was 88,281 short tons, valued at $682,989. This was an increase of 47 per cent in quantity over 1918, but a decrease of about 13 per cent in value.

Graphite in 1919. L. M. Beach. **With a History of Graphite Mining in Pennsylvania.** F. Bascom. Separate from Mineral Resources of the United States, 1919, Part II. 16 pp. Published July 19, 1921. The year 1919 shows marked depression in the graphite industry. The total sales of domestic graphite in 1919 were 7422 short tons, valued at $778,857, a decrease of 43 per cent in quantity and 49 per cent in value from the sales in 1918; but the business done was nevertheless of larger value than in any year prior to 1916.

Fluorspar and Cryolite in 1919. H. W. Davis. Separate from Mineral Resources of the United States, 1919, Part II. 20 pp. Published July 20, 1921. The fluorspar statistics for 1919 show a decrease of nearly 48 per cent in the shipments as compared with 1918, the year in which fluorspar reached its highest recorded output. Notwithstanding the decreased demand for fluorspar in 1919, considerable prospecting and development work were done and several new mines were opened. Nevada was added as a producing state.

All the natural cryolite used in the United States is imported from Greenland. Statistics are given showing the annual imports of cryolite, beginning in 1894 and extending through 1919.

Concrete Stone and Concrete Blocks in 1919. G. F. Loughlin and M. E. McCaslin. Separate from Mineral Resources of the United States, 1919, Part II. 9 pp. Published July 27, 1921.

Advance Statement of the Production of Copper in the United States in 1920. H. A. C. Jenison. 7 pp. 1921. Summaries are given showing the production of copper in the United States in 1913–1920; copper produced in the United States from domestic ores, 1913–1920; world's production of copper (smelter output), 1913–1919, in pounds; primary and secondary copper produced by regular refining plants and imported in 1913–1920, in pounds; stocks of copper January 1, 1906–1921, in pounds; apparent domestic consumption of refined new copper in 1913–1920, in pounds; copper imported into the United States in 1919 and 1920, in pounds; copper exported from the United States, 1919 and 1920, in pounds; brass exported from the United States in 1919 and 1920, and the principal features of the copper industry, 1907–1920.

Manganese Deposits near Bromide, Oklahoma. D. F. Hewett. Bulletin 725-E. Separate from Contributions to Economic Geology, 1921, Part I. 19 pp. Published July 26, 1921.

Routes to Desert Watering Places in the Mohave Desert Region, California. D. G. Thompson. Prepared in coöperation with the Department of Engineering of the State of California. Water-Supply Paper 490-B. 269 pp. 1921. The report contains brief statements regarding the quality of the water of most of the springs and wells, as shown by analyses.

Chrome Ores in Pennsylvania, Maryland and North Carolina. Papers by E. B. Knopf and J. V. Lewis. Bulletin 725-B. Contributions to Economic Geology, 1921, Part I. 55 pp. Published August 4, 1921. Under the stimulus to production caused by war necessities, attempts have been made to revive the production of Maryland and Pennsylvania mines. Two mines were reopened and preparations were made to concentrate the disseminated ores. No large bodies of chrome ore have been discovered in North Carolina, and in view of the swiftness of the mountain streams, it seems likely that no workable deposit will be discovered.

Mineral Resources of Alaska. Report of Progress of Investigations in 1919. A. H. Brooks and Others. Bulletin 714. 244 pp. Paper, 35 cents. 1921. This volume is the sixteenth of a series of annual bulletins treating of the mining industry of Alaska and summarizing the results achieved during the year in the investigation of the mineral resources of the Territory. These reports are intended to give prompt publication of the more important economic results of the year.

Surface Water Supply of the United States, 1918. Part I—North Atlantic Slope Drainage Basins. N. C. Grover, C. H. Pierce, C. C. Covert, and G. C. Stevens. Prepared in coöperation with the States of Maine, Vermont, Massachusetts, and New York. Water-Supply Paper 471. 183 pp. 1921.

Mineral Resources of the United States in 1918. Introduction by E. S. Bastin. Summary by M. B. Clark. Separate from Mineral Resources of the United States, 1918, Part I. 139 pp. Published August 15, 1921. This report contains the statistics of production in the United States in 1918, the imports and exports for that year and for several preceding years, and the records of important new developments during 1918.

Salt, Bromine and Calcium Chloride in 1920. R. W. Stone. Separate from Mineral Resources of the United States, 1920, Part II. 9 pp. Published August 5, 1921. The quantity of salt produced and sold in the United States in 1920 was 6,965,188 short tons, valued at $30,539,168, an increase of only 82,000 lbs. but of nearly $3,500,000 over 1919.

The bromine marketed in 1920 was 37 per cent less in quantity and 40 per cent less in value than in 1919.

The following table shows the calcium chloride produced and marketed in the United States, 1911-1920.

Year	Quantity Short Tons	Value	Average Price per Ton
1911	14,606	$91,215	$6.25
1912	18,550	117,272	6.32
1913	19,611	130,030	6.63
1914	19,403	121,766	6.28
1915	20,535	130,830	6.37
1916	27,709	224,997	8.12
1917	30,503	451,480	14.80
1918	26,621	503,452	18.91
1919	26,123	321,596	12.31
1920	58,604	2,045,851	34.91

Gold, Silver, Copper, Lead, and Zinc in Arizona in 1919. Mines Report. V. C. Heikes. Separate from Mineral Resources of the United States, 1919, Part I. 41 pp. Published August 12, 1921.

The mines of Arizona produced in 1919 ore and placer bullion containing gold, silver, copper, lead, and recoverable zinc valued at $111,157,872. The value of the output, compared with that of 1918, decreased about 45 per cent.

	1918	1919	Decrease in 1919
No. of producers	469	339	130
Ore, short tons	19,038,486	13,727,403	5,311,083
Gold[1]	$5,435,027	$4,506,413	$928,614
Silver,[1] fine ounces	6,686,152	5,266,605	1,419,547
Copper, pounds	764,855,874	538,100,844	226,755,030
Lead, pounds	12,503,689	10,203,078	2,300,611
Recoverable zinc, pounds	2,269,643	1,717,000	552,643
Total value	$202,134,880	$111,157,872	$90,977,008

[1] Includes small placer production.

Gold, Silver, Copper, Lead, and Zinc in Utah in 1919. Mines Report. U. C. Heikes. Separate from Mineral Resources of the United States, 1919, Part I. 33 pp. Published August 9, 1921. The total output of ores of gold, silver, copper, lead, and zinc from mines in Utah was 54 per cent less in 1919 than in 1918, as shown in the following table. This great decrease was mainly in the output of low-grade disseminated copper ore, which was 6,896,493 tons less than in 1918.

	1918	1919	Decrease in 1919	1864–1919
No. of producers	251	179	72	...
Ore, short tons	14,705,718	6,745,423	7,960,295	...
Gold	$2,949,170[1]	$2,159,471	$789,699	$98,227,974
Silver, fine ounces	13,455,597[1]	11,649,961	1,805,636	391,126,085
Copper, pounds	227,169,630	124,061,807	103,107,823	2,313,393,850
Lead, pounds	167,008,224	123,829,051	43,179,173	4,266,437,432
Recoverable zinc, pounds	18,399,417	4,431,024	13,968,393	214,788,050
Total value	$86,047,597	$45,169,328	$40,878,269	$1,047,372,262[2]

[1] Includes small placer production.

[2] The total by years, to the end of 1913, appears in Mineral Resources, 1913, I (1914), 366.

Chromite in 1920. Edward Sampson. Separate from Mineral Resources of the United States, 1920, Part I 8 pp. Published August 17, 1921. A review of the chromite industry for 1920 shows that in many respects pre-war conditions have been reëstablished, though productions show some marked and probably permanent effects of the war.

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, May 1921. W. W. Adams. 8 pp. Paper, 5 cents. 1921.

Coal Mines and Mining. Operating Regulations to Govern Coal-Mining Methods and Safety and Welfare of Miners on Leased Lands on Public Domain, under Act of February 25, 1920. Public 146 (66th Congress). 48 pp. 1st edition, May 1921. Paper, 5 cents.

Laboratory Studies of the Trent Process. G. St. J. Perrott, S. P. Kinney, and O. P. Hood. Reports of Investigations. Serial No. 2263. 18 pp. Issued July 1921.

Separation of Sphalerite, Silica, and Calcite from Fluorspar. John Gross. Reports of Investigations. Serial No. 2264. 3 pp. Issued July 1921.

Sanitation in Planning and Developing Oil-Shale Camps. A. L. Murray. Reports of Investigations. Serial No. 2265. 7 pp. Issued July 1921.

Leaching Iron Ores for Phosphorus. R. M. Winslow. Reports of Investigations. Serial No. 2266. 3 pp. Issued July 1921. Experiments are described on the leaching of iron ores high in phosphorus, to determine whether it was economically possible to reduce the phosphorus content appreciably by leaching. As the research had a practical as well as a theoretical application, only low concentration of acids and alkalies was used.

Slate as a Permanent Roofing Material. Oliver Bowles. Reports of Investigations. Serial No. 2267. 5 pp. Issued July 1921. The purpose of this preliminary paper is threefold. One object is to bring to the attention of slate producers certain modifications in manufacture and classification which would encourage a wider use of slate. A second purpose is to direct the thought of roofers toward the importance of proper laying of slate, and the third purpose is to acquaint the general public with its enduring qualities.

Selection of Analysts for Color Work in Chemistry. H. R. O'Brien. Reports of Investigations. Serial No. 2268. 5 pp. Issued July 1921. Tints were made up similar to those to be used in analysis. Average normal reactions were obtained, and individuals tested. Ranking in these tests was confirmed in subsequent work.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. Reports of Investigations. Serial No. 2269. 28 pp. Issued July 1921.

Articles from the Journal of Agricultural Research

Relation of Hardness and Other Factors to Protein Content of Wheat. H. F. Roberts. **21** (July 15, 1921), 507–22

A Constant-Temperature Bath for Heating Blood Serum. R. R. Henley. **21** (July 15, 1921), 541–4.

Assimilation of Nitrogen, Phosphorus, and Potassium by Corn when Nutrient Salts Are Confined to Different Roots. P. L. Gile and J. O. Carrero. **21** (July 15, 1921), 545–73.

Reduction in the Strength of the Mercuric Chloride Solution Used for Disinfecting Sweet Potatoes. J. L. Weimer. **21** (July 15, 1921), 575–87.

COMMERCE REPORTS—AUGUST 1921

The Comodoro Rivadavia **petroleum** fields are described. (Pp. 602–8)

Freedom of trade in Polish **oil** is announced, effective September 1, 1921. (P. 609)

Germany has been very active during the past year in the Shanghai **dye** trade, and the methods employed for reëstablishing trade have been very effective. (P. 617)

The **chemical trade** in Japan has been compelled to undergo extensive readjustment since the armistice, and all companies have suffered a sharp decline in prosperity. The **soda** industry, which increased more than fourfold during the war, is cited as one of the most prominent illustrations of this decline. (P. 632)

Large deposits of **sulfate of magnesium** and **sulfate of aluminium** are available in Chile. (P. 656)

The summer season of 1921 found the German **potash monopoly** beset by a business stagnation so aggravated by lack of both foreign and domestic orders that some plants are being forced to close down. (Pp. 680–1)

The fact that Formosa has a virtual monopoly of the world's **camphor** supplies and that the quantities arriving from that quarter are gradually diminishing has raised the question as to whether the production of camphor in China can be stimulated. (P. 702)

Valuable deposits of **monazite sand** exist at Bentota, Ceylon, and a sample of the sand analyzed by the Imperial Institute was reported to contain 8.4 per cent of thorium. (P. 703)

A research laboratory has been established at Perth for the purpose of utilizing Australia's forest wealth. Experiments have demonstrated that there exist several forest growths from which a satisfactory **paper pulp** can be made. Investigations are also being pursued relative to **tanning materials**. (Pp. 716–8)

The present position of the Chilean **nitrate** industry is described and it is stated that before the industry, which under normal conditions represents two-thirds of Chile's export trade, can be revived in Chile, some way must be devised to dispose of the high-priced stocks abroad, making way for new shipments and clearing out the accumulation of domestic supplies (Pp 718–9)

Changes in the **petroleum** tax law of Ecuador are cited. (P. 738)

Statistics are given showing the output of **petroleum** in Poland, 1901–1920. Up to the end of 1920 Polish wells produced a sum total of 22,520,600 tons of crude oil. The oil is of two types—a standard type yielding paraffin wax and a special type possessing no wax but containing a greater percentage of motor spirit. (Pp. 740–1)

Restrictions have been removed from the Hongkong **dye** trade. The effect is to remove the prohibition against the importation into Hongkong of foreign dyestuffs and once more to open the trade to all countries. (Pp. 756–7)

The subcommittee appointed to investigate conditions in the dye-making industry of Great Britain has prepared and submitted to Parliament a report outlining a brief history of that industry, the causes of the British loss of trade and the rise of the German industry, the existence of combinations, and the causes of the increase in price for **dyestuffs** as compared with the pre-war level. (Pp. 761–2)

Several thousand tons of good quality **copra** are produced annually in the Solomon Islands, and it is thought that a good opportunity exists for American trade in this product. (P. 771)

The 1920 **oilseed** trade of Hull, England, is reviewed. (Pp. 788–9)

The past year has been a busy one for the **paint and varnish** industry of Hull, England, especially during the first half of the year, when the demand exceeded the supply. (P. 789)

A schedule is given of the Mexican consumption taxes on **petroleum** products. (P. 794)

China is the only country which produces **tea oil** in large quantities. The oil is used by the natives as a medicine. (P. 811)

Recent developments of Tampico **oil fields** are described. Despite claims that Mexican production will rapidly decline, and that the last of the known pool is actually being drained, new gushers continue to be located. (Pp. 817–9)

Finland's **tar and turpentine** industry, 1920, is reviewed. (Pp. 850–2)

The British Empire **oil** situation is briefly outlined. (Pp. 862–3)

One of the new mining regulations in Peru prohibits the granting of any **petroleum** concessions until after the National Congress passes the new petroleum law. (P. 865)

The gradual decline of the Sicilian **sulfur** industry in recent years is clearly shown by the statistics of production, stocks on hand, and export of sulfur from 1897 to 1920:

Years	Production Metric Tons	Stocks on Hand Metric Tons	Exports Metric Tons
1897	443,418	224,860	422,910
1898	465,021	235,022	460,800
1899	521,982	262,087	493,460
1900	516,789	242,438	574,460
1901	537,679	306,903	472,840
1902	501,021	329,836	481,280
1903	536,044	383,524	489,380
1904	499,322	370,606	490,090
1905	538,534	462,865	469,730
1906	475,553	537,588	399,100
1907	403,538	598,709	343,950
1908	404,297	616,419	377,610
1909	402,353	647,880	364,953
1910	397,808	641,249	395,944
1911	376,161	551,422	456,227
1912	356,555	450,917	447,590
1913	345,548	376,365	414,716
1914	334,974	369,001	338,308
1915	319,260	323,860	359,806
1916	233,835	155,372	396,035
1917	177,453	156,800	162,971
1918	194,585	112,050	230,769
1919	181,374	136,859	147,755
1920	219,844	147,886	190,175

(Pp. 874–5)

The value of the **mineral production** of the Province of Quebec for 1909 was $5,552,082. This value has steadily increased, until during 1920 it amounted to $28,223,141. Consul General Albert Halstead, in a recent report, says that the Chamber of Commerce at Montreal states that about 75 per cent of the territory in the Province is unexplored as regards its mineral deposits. The report also states that about 80 per cent of the world's production of asbestos is supplied by that Province. (P. 878)

There is a strong but steady demand in the Malay Peninsula for **boric acid** in powder form for the retail drug trade. (P. 902)

The cost of **tin** mining in the Straits Settlements is described. (Pp. 910–1)

The French **alcohol** production and trade for January–May, 1921, is reviewed. (P. 920)

The Departmental Agricultural office of the Basses-Alpes and the Syndicate of Producers of **lavendar essences** are organizing a sample fair to be opened on October 1, 1921. At this fair will be organized a special congress with the purpose of studying all questions relative to lavendar. (P. 939)

Large deposits of **gypsum** have recently been discovered in Ireland. (P. 960)

Notwithstanding reports at various times of rich **mineral resources** in Syria, operations conducted thus far have not justified such optimistic conclusions. (P. 971)

The principal **vegetable oils** produced in Foochow consular district are tea oil, wood oil, camphor oil and peanut oil. (P. 972)

Statistics are given showing the British trade in **oilseeds** and allied products for the first six months of 1921. (Pp. 1030–1)

Investigations concerning the extent of the **kaolin** deposits in Puolanka, Finland, seem to lead to very favorable results. It has been ascertained that there are at least 10,000 tons and a calculated probability of more than 500,000 tons. (P. 1044)

The first semester of the year 1921 in the **olive-oil** trade of Marseille has been frankly bad. The market has undergone a progressive decline, with continual pauses in expectation of recoveries which have failed to materialize. (P. 1045)

In the Yarmouk Valley in northern Palestine are vast quantities of an oil-impregnated **shale**. When burned this shale leaves a fine quality of lime, which, when air slaked, is said to be very superior for building purposes. (P. 1056)

STATISTICS OF EXPORTS TO THE UNITED STATES

TAMPICO, MEXICO—(Pp. 618, 741)
Petroleum

FINLAND—(P. 623)
Minerals
Asphalt, tar
Oils, greases, wax, and products thereof
Ether
Volatile oils
Colors and dyes
Chemicals, elements and drugs

SANTA MARTA, COLOMBIA—(P. 633)
Cinchona bark

NOVA SCOTIA—(P. 670)
Creosote oil

HALIFAX—(P. 676)
Ammonia, sulfate
Oil, cod

AMSTERDAM—(P. 677)
Creosote oil
Rubber
Paints
Quinine and cinchona bark

UNITED KINGDOM—(P. 729)
Bleaching powder
Salt (not table)

CANADA—(P. 758
Animal products
Iron
Nonferrous metals
Nonmetallic minerals
Chemical products

NORTHERN SYRIA—(Pp. 766–7)
Gum tragacanth
Licorice root

SOERABAYA—(P. 787)
Copra
Rubber

PALERMO, ITALY—(Pp. 856–7)
Chemicals, except coal-tar
  Citrate of lime
  Citric acid
  Mannite
  Tartar, crude
  Tartaric acid
  Wine lees
Crude drugs and essential oils
  Bergamot
  Licorice
  Manna
  Oil of lemon
  Oil of orange
Oil seeds and vegetable oils
  Olive oil, edible
  Sulfur oil

PERU—(P. 876)
Copper bars
Vanadium ore
Copper matte
Other minerals
Cottonseed cake
Hides and skins

HULL, ENGLAND—(P. 790)
Chemicals
  Barium
  Carbolic acid
Coal-tar products
  Anthracene
  Cresol
  Creosote
    Oil
    Saponified
  Naphthalene
Copper
Fertilizer
Oils, vegetable
  Linseed
  Rape
Oil cake meal
Paints, pigments and colors
  Blue wash containing ultramarine
  Marine composition
  Oxide of iron
  Ultramarine
  Lithopone
  Ocher
  Paris white
Rubber
Seeds, castor

LONDON, ENGLAND—(Pp. 860–1)
Tin
Rubber
Creosote oil
Drugs and chemicals
Leather
Aluminium
Hides
Gums
Linseed oil

TAIWAN—(Pp. 882–3)
Camphor

CHINA—(Pp. 922–3
Vegetable tallow

NAPLES, ITALY—(P. 918)
Olive oil
Sulfur (olive) oil

BAHAI, BRAZIL—(P. 966)
Hides and skins
Ipecac root
Chrome ore
Manganese ore

NETHERLANDS—(P. 1002)
Aniline dyes
Chemical preparation for perfumery
Drugs and medicines
Haarlemer oil
Quinine and cinchona bark
Nitrate of soda
Oxalic acid
Plants for medicinal use
Potash
Fertilizers, all kinds

WINNIPEG—(P. 1006)
Cement, Portland
Glycerol, crude
Linseed oil

PALERMO—(P. 1016
Olive oil
Citric acid

BORDEAUX—(Pp. 1019–20)
Aluminium crude
Glycerol
Copal gum
Gum arabic
Rosin gum
Sandaraque gum
Ocher
Prussiate of soda, yellow
Rubber
Silicide of calcium
Tartar, crude

BREST—(P. 1022)
Drugs, crude
Glycerol, crude

CALAIS—(P. 1022)
Petroleum products
Mineral products
Wood pulp

SHANGHAI—(Pp. 1028–9)
Antimony
Albumin
Camphor
Oil, wood
Linseed
Sesame seed

AUSTRIA—(P. 1046
Rubber
Ores, metals
Pigments, paints and varnishes
Tin and zinc
Nickel

HAVRE—(Pp. 1048–9)
Aluminium
Copper
Drugs
Dyestuffs
Glues
Iridium, crude
Oil (for soap manufacture)
Palladium, crude
Platinum, crude
Potash
Rubber
Soda, prussiate of

LYONS—(Pp. 1054–5
Chemicals, drugs and dyes
Oils, essential
Tartar

CZECHOSLOVAKIA P. 1055)
Chemicals

BOOK REVIEWS

Plantation Rubber and the Testing of Rubber. By G. STAFFORD WHITBY, Ph.D., M.Sc., A.R.C.Sc., Associate Professor, Department of Chemistry, McGill University, Montreal, Canada. xvi + 559 pp. Longmans, Green & Co., London and New York, 1920. Price, $9.50 net.

This volume of the group of scientific monographs, edited by Sir Edward Thorpe, fully justifies the editor for his choice of subject and author. Within the field covered, the previous work has been carefully studied and presented in great detail. While appealing largely to the technical men concerned with the cultivation, it is likely to prove of considerable value to the consumers of crude rubber. Not since the classic work of C. O. Weber in 1902 has there been any publication on the subject which at all compares with this volume with respect to the multiplicity of authorities consulted, the careful consideration of the evidence presented, and, in general, the soundness of the conclusions drawn from the facts.

Whitby has confined himself to the field of plantation rubber, and even that portion of the work which covers the testing of rubber is studied largely from the work of the plantation laboratories.

Part One deals with the various problems connected with the growth and cultivation of the tree, the collection and coagulation of the latex, and the preparation of the crude rubber. Chapter IX deals with the variation in the quality of plantation rubber, and, while it undoubtedly represents the best work which has been done up to this time, it is not all that one might desire from the consumer's point of view. It is obvious that only at the plantations could a study be made of such variations, caused by any one of the many variables which arise during the production of the rubber. It is, however, decidedly unfortunate that most of this work has been undertaken by men who are not as familiar as they might be with the practical use of the product. This has resulted in a narrowness of research which has led to the drawing of many conclusions on insufficient evidence. Instead of the variation in the quality of the rubber itself, we have largely the variation in minute amounts of impurities, whose effect is easily nullified under the present system of manufacture of rubber articles.

Part Two deals with the testing of crude rubber. Practically all of the conclusions as to the best methods of testing are derived from data on compounds of pure gum and sulfur only. While these data are of value, the conclusions drawn from such a narrow field of experimentation must be held to be tentative, pending confirmation on a wider scale with more practical mixtures of rubber, sulfur, and the various commercial ingredients of rubber mixtures. It is not at all obvious that what is true of rubber-sulfur mixtures will also be true of the more complex ones.

Whitby has raised a very interesting point in suggesting the adoption of stress-strain curves in place of recording merely the maximum values. Minute flaws greatly decrease the maximum values and make comparisons between two samples extremely uncertain. Whitby contends that the curves for two or more test pieces from the same sheet will coincide up to the point of break, although some test pieces will carry on the curves to higher breaking loads and elongation.

Standardization of these stress-strain curves is desirable as Whitby has pointed out (footnote, p. 223), but it can hardly be said that Whitby has succeeded in accomplishing very much in this direction. Some of the charts have their zero point at the lower left, and some at the lower right side of the figure. In his own work, he plots strains along the ordinates, whereas in reproducing work of others he sometimes plots stresses on the ordinates. No doubt all of these could have been redrawn to a uniform standard and scale. Standardization of nomenclature would further simplify matters: elongation, strain, and L/B are used for the same quantity, while stress, load, and P/B are also used interchangeably. Some charts are in the metric system and some in the English. There can at least be no justification for using "kg. per cm.^{2}" and "kg. per mm.^{2}" for the same quantity. Since charts are merely to facilitate comparison of results, the necessity for uniformity of practice and nomenclature is apparent.

The volume also contains an excellent bibliography, and an adequate index.

JOHN B. TUTTLE

Applied Colloid Chemistry—General Theory. WILDER D. BANCROFT, Professor of Physical Chemistry at Cornell University. 345 pp., 10 figures. McGraw-Hill Book Co., Inc., New York, 1921. Price, $3.00.

The inhabitants of the Tower of Babel had much to be thankful for in comparison with scientific research workers in this age of extreme specialization. We welcome, therefore, with enthusiasm a work which teems with ideas and suggestions as to how data and information acquired in one field may be applied effectively to a wide range of other fields. Bancroft has done this and more. In a book of less than three hundred and fifty pages he has accumulated and coördinated a mass of data and information worthy of a dictionary or encyclopedia, which will insure its use as a work of reference. But what is more important, he has put these data together in a consecutive manner, developing the subject deductively rather than empirically, making the whole such interesting reading that it would be difficult to open tha book at any point without encountering some stimulating idea or suggestion.

After reading this book one's first inclination is to ask for more of the same sort. It is a relief therefore to learn from the preface that this work is simply introductory and is to be followed by a series of special volumes dealing more intimately with a variety of technical and scientific fields. In a characteristically Bancroftian manner the suggestion is made that since the author is not likely to be able to produce the volumes in question more rapidly than one in three years, it might be advisable for others to coöperate in the grand scheme.

Perhaps the most striking feature of this book is the fearless way in which data are weighed and criticized and much chaff that has passed for grain in previous textbooks is shown up for what it is worth. The whole structure is put together in a consecutive, coherent form which should reduce this comparatively new science of colloidal chemistry from its nebulous state to a form in which it will no longer be the despair of exact philosophers.

This work should prove extremely suggestive not only to all sorts and conditions of chemists but also to physicists, engineers, geologists, biologists, and medical men.

The subjects covered include Adsorption of Gas or Vapor by Solid; Adsorption of Vapor by Liquid; and of Liquid and Solid by Solid; Adsorption from Solution; Surface Tension-Brownian Movements; Coalescence; Preparation of Colloidal Solutions; Properties of Colloidal Solutions; Jellies and Gelatinous Precipitates; Emulsions and Foams; Nonaqueous Colloidal Solutions; Fog and Smoke; Gases and Solids in Solids; Thickness of Surface Films, and particularly detailed Author and Subject Indexes.

The following quotation serves as a typical illustration of the painstaking detail of treatment found throughout the book:

> Silver yields a beautiful yellow color when applied to glass as a surface stain. This is the color of colloidal silver solutions

having the finest particles. * * * * In the case of enamels silver is added to the mass of the glaze and not as a surface stain. Addition of silver carbonate together with bismuth oxide gives rise to an intense blue. One function of the bismuth oxide is to hold the silver to the body, but it must also cause a partial agglomeration of the silver because the lustres are blue to green instead of yellow to brown. A yellow stain of silver on a cobalt blue enamel gives a green. This is a ceramic analogue of the tree frog.

The subject of blue eyes and blue feathers with which Bancroft has delighted many an audience is handled in his usual effective manner.

Bancroft rambles cheerfully from the boudoir, with such information as "It seems probable that the possibility of using face powder is merely a special case of a very fine powder adhering to a curved surface," to the kitchen with "I have been told that Béarnaise sauce is an emulsion of melted butter in tarragon vinegar without any egg and that it is made very easily. If this is so, tarragon vinegar must contain a good deal more of some emulsifying agent, probably a tannin, than ordinary vinegar."

Biologists would do well to read the paragraphs discussing osmotic phenomena from the standpoint of negative adsorption in pores; solutions in continuous films; and the release of acids from neutral salts by means of fuller's earth which latter phenomena, in the reviewer's opinion, throw much light on the problem of acid secretion in the stomach.

We refer those who enjoy Bancroft's characteristic humor to the paragraph on the iodine starch reaction on page 111, and his discussion of Langmuir's theories regarding adsorption on page 38.

In conclusion it may be said that Bancroft has proved once more that he is incapable of being dull. He has handled a heterogeneous mass of disconnected, dry-as-dust data in a manner calculated to add something to the joy of thinking, if not of living, for us all.

G. H. A. Clowes

Benzol, Its Recovery, Rectification, and Uses.[1] By S. E. Whitehead. 22 × 14 cm. xiv + 209 pp. D. Van Nostrand Co. New York, 1920. Price, $5.00.

The benzol recovery industries of England and America must be counted among the permanent benefits left in the wake of the great war. "War," writes Lord Moulton in an appreciative Introductory Note to this book, "is a long and disheartening tale of the destruction of that which the human race has accumulated by its industry and labor. * * * But, like all other concentrations of human effort, it brings with it some return in the way of new experience and wider knowledge, and it is our duty to take care that this gain is not allowed to escape us." Mr. Whitehead's book is valuable in perpetuating an important part of such experience and knowledge.

The opening sentence of the preface indicates one of the fundamental points of difference between British and American benzol recovery practice: "This volume is intended as a guide in the principles and practice of benzol recovery, chiefly applied to gas works." In America, benzol is essentially a product of the by-product coke oven. Economic conditions do not warrant its recovery from domestic gas except under such unusual circumstances as those of the great war. Benzol is worth more to the American gas works as gas than as motor fuel. With gas of 550 B.t.u. per cu. ft. selling for $1.20 per M cu. ft., 100,000 B.t.u. in the form of gas are worth 21.8 cents. With benzol of 132,100 B.t.u. per gallon selling at 25 cents per gallon, 100,000 B.t.u. in the form of motor fuel are worth 18.9 cents.

In England, on the other hand, the price of gas is about the same as here, while motor fuel commands twice the American price. This difference, together with the general adoption of lower calorific standards for gas, favors the recovery of benzol in British gas works as well as in the coke plants. It appears, however, that in his enthusiasm over his subject the author has somewhat exaggerated the real value of benzol recovery to the gas manufacturer. On page 15, he states, "When gas is sold at 5s. per 1000 cu. ft., the value of 1 gallon of crude benzol sold as gas is 2d." This incredible statement is at variance with Mr. Whitehead's further calculations on page 127 and can be accounted for only by assuming that he has estimated 1 cu. ft. of benzol vapor to be worth no more than 1 cu. ft. of illuminating gas. Turning now to page 127, we find the calculation made on a more proper basis, but even here there seems to be a stretching of figures to prove the point. "The supply of 500 B.t.u. gas at 4s. 0d. per 100 cu. ft. is equivalent to selling 100,000 B.t.u. for 9.5d. On this basis, a gallon of crude benzoi would represent about 11d. since 75 to 80 per cent of it is extracted from the gas." Even on a 4s. basis one gallon of crude benzol is worth more than 11d. It is necessary to figure the difference in the total B.t.u. salable as gas per ton of coal with and without benzol recovery. Table 8 shows this difference to be 446,300 B.t.u. for 3 gallons recovered per ton, or about 148,800 B.t.u. per British gallon[1] of benzol. If 100,000 B.t.u. are worth 9.5d., the removal of each gallon of crude benzol must be charged with 14d., representing its value in the form of gas. The efficiency of recovery here makes no difference, contrary to what the author appears to suppose. Adding a recovery cost of 4d. per gallon, the cost of one gallon of crude benzol to the gas works amounts to 1s. 6d. Figures recently published by the National Benzole Co., Ltd., assume 1s. 4d. per gallon of crude benzol and estimate a net cost of 2s. 3d. per gallon of motor fuel at the manufacturer's works. Taking distribution charges into account, it can be seen that with motor fuel selling at 3s., there is no excessive margin of profit to the gas manufacturer.

Comparing British benzol recovery practice, as outlined in Mr. Whitehead's book, with that developed in America, the relation to gasworks operations in the former case is seen to have no small influence. The British plants are more numerous and smaller than those in America. In America, the plants are all of very similar design, while in England there is offered a considerable variety of apparatus and process.

Another fundamental point of difference between British and American practice lies in the use of coal-tar oils and blast-furnace creosote as absorbents in England, as compared with the universal use of petroleum oils in America. The reviewer is convinced that American practice is better favored in this regard. The trouble with absorption of sulfur and corrosion which Mr. Whitehead describes as attending the use of paraffinoid oils has not been noticed to any appreciable extent here.

Part I deals with the recovery of crude benzol. One of the most interesting and valuable features of the book is the exposition of theoretical principles. The dependence of benzol recovery upon considerations of vapor pressure deserves careful study by all who desire to acquire a thoroughly scientific knowledge of the subject.

The recovery of benzol from carbureted water gas receives only a passing reference. Although carbureted water gas is not manufactured in as great proportion to coal gas in England as in America, the great developments made in this country in the recovery of toluene from this source during the war deserve description.

Part II deals with the rectification of benzol. Part III has four chapters on the uses of benzol and its products, the most interesting of which is the chapter on benzol as motor fuel.

Among those sections of the book of least value to the American reader, the reviewer regrets to include the descriptions of analytical methods. Any American chemist familiar with the subject will appreciate the great superiority of the methods developed in this country during the war. It is to be regretted that most of the descriptive matter relating to these is still scattered through periodical literature or has not even been published, but this deficiency will soon be made up in the publication of the second edition of the "Gas Chemists' Handbook."

---

[1] Editor's Note: The use of the term "benzol" by the author of the above book has made it necessary to suspend the rule of the American Chemical Society regarding nomenclature in this instance.

[1] The reader is to be cautioned to avoid confusing the British Imperial gallon with the American gallon. There is a tendency to such confusion in some of the quotations from American literature given by Mr. Whitehead. in which the difference of units is not clearly pointed out.

Mr. Whitehead's book is to be highly commended for its attention to practical detail. The description of the apparatus employed for gas scrubbing, wash oil distillation, benzol washing and rectification is the best that has appeared in any technical literature. More space than usual is given to cost calculations. Much attention is paid to matters of practical operation, "shop kinks," precautions and difficulties in work. The book should be owned not only by those who are dealing directly with benzol, but by everyone who is interested in gas manufacture and by-product recovery.

F. W. Sperr, Jr.

Ceramics. A Manual for Chemists, Engineers, and Manufacturers. A. Malinovzsky. 274 pp. D. Van Nostrand Co., New York, 1921. Price $3.00.

This small volume is an attempt to produce a handbook similar to the "Sprechsaal Kalender." The attempt is laudable but has not resulted satisfactorily, for the book has not only all of the faults of the Kalender but a considerable number of its own. In common with the German handbook the arrangement of the subjects is far from being systematic. The information given throughout the book is lacking in accuracy, of which notable examples are the sections on clays, molding and drying, burning, glazes, fritting, refractories, casting, and enamels. The subject of qualitative analysis should have been omitted in a book of this kind. The ceramic calculations are not as useful as those found in the Manual of the American Ceramic Society or in the book by Jackson. In the computation of synthetic glaze compositions the calculations are not carried to the final batch mixtures, as is necessary in practice. Subjects like the Bischof refractory quotient should not have been introduced. The tables of chemical formulas and molecular weights might have been made more useful by the introduction of the factors applied in the computing of ceramic compositions. Such errors as giving the melting point of orthoclase at 1350° C., or cone No. 11, are scarcely permissible. The book is disfigured by numerous misprints. It would seem that the volume will prove to be of only slight value to ceramists, and in no sense can it be said to represent the present status of ceramic information, even approximately. Its defects are many and it is inadequate and unreliable.

A. V. Bleininger

Traité de la Conservation et de l'Amelioration des Bois. (Treatise on the Preservation and Improvement of Wood.) By Maurice de Keghel, Chemical Engineer, Director of the Guido Laboratories, formerly Director of the Wood Preserving Plant of the Companie Francaise. 360 pp. 41 illustrations. J. B. Baillière et Fils, Paris, 1921. Price, 15 fr.

The inroads of the Great War on timber supplies having resulted in a tremendous wood shortage in France, the writer has prepared this small but rather encyclopedic work in order to assist as far as possible in conserving the material at hand.

The book discusses all phases of the injection of wood with reference to the prevention of decay, mineralization in order to render it more resistant to wear, coloring to simulate the more expensive exotic timbers such as rosewood, ebony, etc., waterproofing to prevent warping and checking, aging or senilization, and fireproofing. Information on the manufacture of plywood, veneers, bent wood, composition board, etc., is also given.

As far as Continental conditions go, the subject matter appears rather exhaustive, but the discussion of American methods which the author has attempted leaves much to be desired, as he has little idea of the magnitude of the wood preserving industry in the United States. However, in one place or another he has mentioned most of the commercial processes employed.

Under each principal heading he develops the subject first from a historical standpoint, listing and briefly describing the various methods and patents and showing their defects, the whole discussion leading up to more improved methods which he advocates, and which in several cases are protected by his own patents.

His impregnating apparatus (French Patent 253,201) is in the form of a horizontal steel cylinder built up in unit sections. The simplest type has a hollow conical steel cap centered at either end, the front cap being horizontally adjustable by a long screw projecting through the hinged door in front so as to accommodate varying lengths of timber. The single stick of timber, preferably peeled, is clamped between the two conical caps, the ends being "nosed" to make a tight joint.

The treating process consists in filling the cylinder surrounding the stick with the treating solution at the desired pressure. Simultaneously with this, and at the same hydraulic pressure, the same solution is introduced into the front cap and forced through the stick in a longitudinal direction. The conical cap at the opposite end of the stick is provided with an outlet to take care of the expressed sap. The bath under pressure, surrounding the stick, is mainly for the purpose of balancing internal stresses in the wood due to the pressure applied at the end.

The largest cylinder described is 38 feet long and will accommodate 12 sticks, the equivalent of 48 ties. All treatments are carried out *en masse*, the wood being cut to commercial size, wherever necessary, after treatment.

For treating ties the writer recommends the following formula:

Gelose (agar agar)	1 part
Formaldehyde	1 part
Potassium ferrocyanide	2 parts
Water	100 parts

The theory is that the agar condenses under the action of the aldehyde, becoming insoluble in water and impermeable to crystalloids. The toxic agent is incorporated as a poison to fungi and insects. Service tests on ties, particularly in Brazil where termites and decay were severe, proved the treatment far superior to creosote. The cost of treatment in France is said to be considerably less than for a good creosote treatment.

The treatment recommended for paving blocks where decay is secondary to wear consists in the use of ammonium sulfate followed by calcium sulfate, which forms an insoluble double sulfate of calcium and ammonium, which greatly decreases the permeability of the blocks to water and hardens them.

For treating wood against the teredo the gelose process with the addition of copper sulfate, zinc chloride and phenol, followed by a bath in neutral stearin soap, is recommended. This preserved piling in the Adriatic for at least six months.

For fireproofing wood the writer prefers a basic zinc-ammonium phosphate. This is prepared by dissolving freshly precipitated zinc hydroxide in ammonium hydroxide and adding phosphoric acid. This is soluble in the presence of ammonium hydroxide, but when the ammonia leaves the wood it becomes practically insoluble. Practical fire tests demonstrated its efficiency.

There are 68 pages of discussion on the coloring of wood with various dyes, and many formulas are given.

The drying of impregnated wood in a recirculating kiln of the writer's design and cost data on the installation of a plant to handle various kinds of material are discussed in the last two chapters.

On the whole this is a very valuable treatise, which should be translated into English for the use of our own industries.

C. J. Humphrey

NEW PUBLICATIONS

Celluloid: Its Raw Material, Manufacture, Properties and Uses. Fr. Böckmann. Translated from the German. 2d English revised edition. 188 pp. Illustrated. Price, 9s. 3d. postpaid. Scott, Greenwood & Son, London.

Colorimetric Analysis. F. D. Snell 150 pp. Illustrated. Price, $2.00. D. Van Nostrand Co., New York.

Dictionary of Applied Chemistry. Sir Edward Thorpe. Revised and enlarged edition. Illustrated. Vol. I. 951 pp. Price, $20.00. Vol. II. 717 pp. Price, $20.00. Longmans, Green & Co., New York.

Electric Furnace. J. N. Pring. (Monographs on Industrial Chemistry.) 485 pp. Illustrated. Price, 10.50 net. Longmans, Green & Co., New York.

Explosives: Technical Records of Explosives Supply 1915–1918. No. 2. Manufacture of Trinitrotoluene (TNT) and Its Intermediate Products. Ministry of Munitions and Department of Scientific and Industrial Research. His Majesty's Stationery Office, London, England.

Microbiology: Laboratory Manual in General Microbiology. Prepared by Laboratory of Bacteriology and Hygiene, Michigan Agricultural College. 2d edition. 472 pp. Illustrated. Price, $3.50. John Wiley & Sons, Inc., New York.

Silver Bromide Grain of Photographic Emulsions. A. P. H. Trivelli and S. E. Sheppard. Monographs on the Theory of Photography from the Research Laboratory of the Eastman Kodak Co. No. 1. Illustrated. 143 pp Price, $2.50. D. Van Nostrand Co., New York.

Soaps and Proteins: Their Colloid Chemistry in Theory and Practice. Martin H. Fischer. 272 pp. 114 figures. Price, $4.00. John Wiley & Sons, Inc., New York.

Steel: The Working of Steel. Fred H. Colvin and K. A. Juthe. 244 pp. 123 illustrations. Price $3.00. McGraw-Hill Book Co., Inc., New York

Sulfuric Acid: American Sulfuric Acid Practice. Philip De Wolf and E. L. Larison. 1st edition. 270 pp. Illustrated. Price, $3.50. McGraw-Hill Book Co., Inc., New York.

Thermodynamics. J. E. Emswiler. 266 pp. 124 illustrations. Price, $3.00. McGraw-Hill Book Co., Inc., New York.

Transactions of the American Institute of Chemical Engineers. Vol. XXIII. Part I. (1920) 463 pp. Published by American Institute of Chemical Engineers and for sale by D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES

Ammonia: Le Crude Ammoniac. P. Waguet. *La Revue des Produits Chimiques*, Vol. **24** (1921), No. 13, pp. 399–401.

Analytical Determination of Basicity Figures. James E. Pickering. *Journal of the Society of Leather Trades' Chemists*, Vol. **5** (1921), No. 6, pp. 177–83.

Cellulose: Research on the Fluorescence of Cellulose and Its Derivatives. Samuel Judd Lewis. *Journal of the Society of Dyers and Colourists*, Vol. **37** (1921), No. 8, pp. 201–04.

Charcoal: Briquetting of Charcoal. A. F. Joseph and B. W. Whitfield. *Journal of the Society of Chemical Industry*, Vol. **40** (1920), No. 16, pp. 190*t*–92*t*.

Chaulmoogra Oil: The Chemistry and Therapeutic Properties of Chaulmoogra Oil. L. E. Warren. *Journal of the American Pharmaceutical Association*, Vol. **10** (1921), No. 7, pp. 510–21.

Chemical Factors in Fatigue. I.—The Effect of Muscular Exercise upon Certain Common Blood Constituents. Norris W. Rakestraw. *Journal of Biological Chemistry*, Vol. **47** (1921), No. 3, pp. 565–91.

Chemical Factors in Nutrition. Lafayette B. Mendel. *Journal of the Franklin Institute*, Vol. **192** (1921), No. 1, pp. 1–10.

Chemical Research for the Development of Industries in India. E. R. Watson. *Journal of Indian Industries and Labour*, Vol. 1, Part 2, pp. 183–95; *The Chemical Age* (London), Vol. **5** (1921), No. 115, pp. 234–37.

Coal: Factors in the Economic Selection of Coal. A. L. Booth. *The Coal Industry*, Vol. **4** (1921), No. 7, pp. 347–50.

Coke-Oven: Determination of Benzol in Coke-Ovens. A. Thau. *Blast Furnace and Steel Plant*, Vol. **9** (1921), No. 8, pp. 474–76. Translated from *Gluckauf*.

Dyes: The Bichromates and Wool Dyeing. I. Winthrop C. Durfee. *American Dyestuff Reporter*, Vol. **9** (1921), No. 10, Section 2, pp. 20–23.

Dyes Derived from Phenanthraquinone. Edwin Roy Watson and Sikhibhushan Dutt. *Journal of the Chemical Society*, Vol. **119** (1921), No. 706, pp. 1211–21.

Dyes: The Manufacture of Malachite. Joseph R. Minevitch. *Color Trade Journal*, Vol. **9** (1921), No. 3, pp. 114–18.

Dyes: Scroopy Effects on Cotton, Woolen and Silk Goods, with Possible Future Changes. Raffaele Sansone. *Textile Colorist*, Vol. **43** (1921), No. 513, pp. 591–95.

Electrometric Control in Chemical Industry. Eric K. Rideal. *The Chemical Age* (London), Vol. **5** (1921), No. 115, pp. 232–33.

Fat-Splitting Reagents from Cymene. R. H. McKee and L. J. Lewis. *Chemical Trade Journal and Chemical Engineer*, Vol. **69** (1921), No. 1787, pp. 211–13. From *American Perfumer and Essential Oil Review.*

Fertilizers: A Protection in War but Promoters of Peace. William H Waggaman. *The American Fertilizer*, Vol. **55** (1921), No. 4, pp. 33–41.

Flotation: Surface-Energy and Adsorption in Flotation. A. W. Fahrenwald. *Mining and Scientific Press*, Vol. **123** (1921), No. 7, pp. 227–34.

Fuel: Anthracoal: A New Domestic and Metallurgical Fuel Made by Coking Anthracite Fines with Coal-Tar Pitch. Donald Markle. *Coal Age*, Vol. **20** (1921), No. 8, pp. 296–99.

Glass: The Influence of Aluminium on the Properties of Glass. Violet Dimbleby, F. W. Hodkin and W. E. S. Turner. *The Glass Industry* Vol **2** (1921), No. 9, pp. 216–19.

Glass: Water Problems in Glass Manufacture. William Macklin Taylor. *The Glass Industry*, Vol. **2** (1921), No. 9, pp. 209–13.

Hydrogen-Ion: Notes on the Measurement of Hydrogen-Ion Concentration. G. W. Monier-Williams. *The Analyst*, Vol. **46** (1921), No. 545, pp. 315–24.

Iron: Chemical Reactions in Foundry Cupolas. Y. A. Dyer. *The Iron Age*, Vol. **108** (1921), No. 5, pp. 259–62.

Kaolins: Absorption of Sodium Hydroxide by Kaolins. R. F. Geller and D. R. Caldwell. *Journal of the American Ceramic Society*, Vol. **4** (1921), No. 6, pp. 468–73.

Laboratories: Les Laboratoires Industriels. E. R. Simonnet. *L'Industrie Chimique*, Vol. **8** (1921), No. 91, pp. 302–06.

Laboratories: The Textile Laboratory and Its Equipment. Charles L. Howarth. *American Dyestuff Reporter*, Vol. **9** (1921), No. 10, Section 2, pp. 33–35.

Lime: The Rotary Kiln for Lime Burning. J. G. Jones. *Concrete*, Vol. **19** (1921), No. 2, pp. 111–14.

Nickel: Survey of Nickel Solutions. Joseph Haas, Jr. *The Metal Industry*, Vol. **19** (1921), No. 9, pp. 364–66.

Nitrocellulose: The Chemistry, Manufacture and Uses of Nitrocellulose. Hugo Schlatter. *Chemical and Metallurgical Engineering*, Vol. **25** (1921), No. 7, pp. 281–86.

Oil-Shale: Distillation of Oil-Shale. David E. Day. *Mining and Scientific Press*, Vol. **123** (1921), No. 8, pp. 257–62.

Phosphates: Briquetting Mineral Phosphates. William H. Waggaman, H. W. Easterwood and T. B. Turley. *Chemical and Metallurgical Engineering*, Vol. **25** (1921), No. 11, pp. 517–22.

Rosin: Hardened Rosin and Resin Esters. Alexander Murray. *Chemical and Metallurgical Engineering*, Vol. **25** (1921), No. 10, pp. 473–75.

Rubber: Air Conditioning in Rubber Manufacture. J. Esten Bolling. *The Rubber Age*, Vol. **9** (1921), No. 10, pp. 375–78.

Rubber: Experimental Vulcanization on the Small Scale. D. F. Twiss and S. A. Brazier. *The Rubber Age*, Vol. **9** (1921), No. 9, pp. 337–38.

Rubber: The Mechanism of Action of Certain Accelerators of Vulcanization. G. Bruni and E. Romani. *The India-Rubber Journal*, Vol. **62** (1921), No. 2, pp. 17–20.

Rubber: Sols and Gels of Vulcanized Rubber. Henry P. Stevens. *Journal of the Society of Chemical Industry*, Vol. **40** (1921), No. 16, pp. 186*t*–90*t*.

Rubber: Ten Years' Experience with Aging Tests. William C. Geer and Walter W. Evans. *India Rubber World*, Vol. **64** (1921), No. 6, pp. 887–92.

Steel: Effect of Overheating High Carbon Steel. Lancelot W. Wild. *Blast Furnace and Steel Plant*, Vol. **9** (1921), No. 9, pp. 541–42.

Steel: Heat Treatment of Screw Stock. A. A. Blue. *Blast Furnace and Steel Plant*, Vol. **9** (1921), No. 9, pp. 553–55.

Steel: New Discussion on the Physics of Steel. William R. Webster. *Blast Furnace and Steel Plant*, Vol. **9** (1921), No. 9, pp. 555–63.

Sugar: The Comparative Values of Decolorizing Carbons. A. B. Bradley. *International Sugar Journal*, Vol. **23** (1921), No. 272, pp. 455–61.

Sulfur Removal by Oil Washing. E. R. Hamilton. *American Gas Journal*, Vol. **115** (1921), No. 9, pp. 182–83, 189.

Tar Oils: Uses for Low-Temperature Tar Oils. F. P. Coffin. *Gas Age-Record*, Vol. **48** (1921), No. 3, pp. 97–100.

Terra Cotta: The Value of Aging the Terra Cotta Body. R. L. Clare and R. N. Long. *Journal of the American Ceramic Society*, Vol. **4** (1921), No. 6, pp. 453–58.

Vitamines: Methods Used in the Detection and Investigation of Vitamines. E. Marion Delf. *Journal of the Chemical Metallurgical and Mining Society of South Africa*, Vol. **21** (1921), No 10, pp. 178–83.

Vitamine Studies. VIII—The Effect of Heat and Oxidation upon the Antiscorbutic Vitamine. R. Adams Dutcher, H. M. Harshaw and J. S. Hall. *Journal of Biological Chemistry*, Vol. **47** (1921), No. 3, pp. 483–88.

Waste: Economic Importance of Waste Products Utilization. Walter H. Dickerson. *Chemical Age*, Vol. **29** (1921), No. 9, pp. 339–42.

Water in Relation to Dyeing. John MacGregor. *Color Trade Journal*, Vol. **9** (1921), No. 2, pp. 43–48.

Wool: Constituents of Raw Wool in Relation to Scouring. John MacGregor. *Color Trade Journal*, Vol. **9** (1921), No. 3, pp. 97–102.

MARKET REPORT—SEPTEMBER, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Sept. 1	Sept. 15
Acid, Boric, cryst., bbls	lb.	.12¾	.12¾
Hydrochloric, com'l, 20°	lb	.01½	.01½
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07¼	.07¼
Phosphoric, 50% tech	lb	.12	.12
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	18.00	18.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb.	*.03½	*.03½
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	*.06¾	*.06¾
Ammonia Water, carboys, 26°	lb.	.08	.08
Arsenic, white	lb.	.06½	06½
Barium, Chloride	ton	*46.00	*45.00
Nitrate	lb.	*.08¼	*.07¾
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works,	100 lbs.	2.25	2.25
Borax, cryst., bbls	lb.	.05¾	05¾
Bromine, pure	lb.	.27	.25
Calcium Chloride, fused	ton	28.75	28.75
Chalk, precipitated, light	lb.	.03½	.03½
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.37½	5.37½
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.50	3.50
Lead Acetate, white crystals	lb.	.12	.12
Nitrate	lb.	.15	.15
Red American	100 lbs.	.11¼	.11½
White American	100 lbs.	.09½	.09½
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	*1.40	*1.40
Magnesium Carbonate, tech	lb.	.10	.10
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*43.00	*42.00
Phosphorus, yellow	lb.	.30	.30
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.11½	.11½
Bromide, imported	lb.	*.17	*.16
Carbonate, calc., 80–85%	lb	.05	05
Chlorate, cryst	lb.	*.07½	*.06½
Hydroxide, 88–92%	lb.	*.04¼	*.04¼
Iodide, bulk	lb.	2.75	2.75
Nitrate	lb.	10	.10
Permanganate, U. S. P.	lb.	*.24	*.22
Salt Cake, bulk	ton	20.00	20.00
Silver Nitrate	oz.	.42½	.42½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.15	2.15
Caustic, 76%	100 lbs	3.90	3.90
Sodium Acetate	lb.	.04¾	.04
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.08	.08
Chlorate	lb.	.07½	.07½
Cyanide	lb.	.20	.20
Fluoride, technical	lb.	*.10	*.10
Hyposulfite, bbls	100 lbs.	3.50	3.50
Nitrate, 95%	100 lbs.	2.00	2.25
Silicate, 40°	lb.	.01½	.01½
Sulfide	lb.	.06	.06
Bisulfite, powdered	lb.	.06	.06
Strontium Nitrate	lb.	.12	.12
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride	lb	.18	.18
Oxide	lb.	.40	.40
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.09	.09

ORGANIC CHEMICALS

		Sept. 1	Sept. 15
Acetanilide	lb.	*.28	*.29
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.10	.10
Acetylsalicylic	lb.	.60	.60
Benzoic, U. S. P., ex-toluene	lb.	.65	.65
Carbolic, cryst., U. S. P., drs	lb	.09	.09
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	*.45	*.45
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.16	.15½
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	*.19	*.19
Tartaric, crystals, U. S. P.	lb.	.27	*.27
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12½	.12½
Alcohol, denatured, complete	gal.	.35	.35
Ethyl, 190 proof	gal.	4.75	4.75
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap, refined	lb.	.72	.72
Carbon Bisulfide	lb.	.06	.06
Tetrachloride	lb.	.10½	.10½
Chloroform, U. S. P.	lb.	*.38	*.38
Creosote, U. S. P.	lb.	40	40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.85	2.85
Imported Potato	lb.	.07	.07
Ether, U. S. P., conc., 100 lbs.	lb.	.16	.16
Formaldehyde	lb.	*.12	*.11
Glycerol, dynamite, drums	lb.	.12½	.12½
Methanol, pure, bbls	gal.	1.25	1.25
Pyridine	gal.	2.75	2.75
Starch, corn	100 lbs.	2.28	2.28
Potato, Jap	lb.	.05	.05
Rice	lb.	.18	.18
Sago	lb.	.04½	04½

OILS, WAXES, ETC.

		Sept. 1	Sept. 15
Beeswax, pure, white	lb.	.40	.37
Black Mineral Oil, 29 gravity	gal	.22	.22
Castor Oil, No. 3	lb.	.08¾	.08¾
Ceresin, yellow	lb.	.08½	08½
Corn Oil, crude, tanks, mills	lb.	.07	.07¼
Cottonseed Oil, crude, f. o. b. mill	lb.	.07	.07¾
Linseed Oil, raw (car lots)	gal.	.73	.75
Menhaden Oil, crude (southern)	gal.	.25	.25
Neat's-foot Oil, 20°	gal.	1.00	1.00
Paraffin, 128–130 m. p., ref	lb	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.40	5.55
Rosin Oil, first run	gal.	35	.35
Shellac, T. N.	lb	.44	.53
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.09½	.10½
Tallow Oil, acidless	gal.	.65	65
Tar Oil, distilled	gal	.60	.60
Turpentine, spirits of	gal.	65	.70

METALS

		Sept. 1	Sept. 15
Aluminium, No. 1, ingots	lb.	.20	.20
Antimony, ordinary	100 lbs.	4.50	4.50
Bismuth	lb.	1.50	1.50
Copper, electrolytic	lb	.12	.12
Lake	lb.	.12	12
Lead, N. Y.	lb.	.04½	.04½
Nickel, electrolytic	lb	.41	.41
Platinum, refined, soft	oz.	72.00	78.00
Quicksilver, flask	75 lbs. ea.	*43.00	*42.00
Silver, foreign	oz.	.62	.62
Tin	lb.	.26	.26
Tungsten Wolframite	per unit	3.25	3.25
Zinc, N. Y.	100 lbs.	4.50	4.50

FERTILIZER MATERIALS

		Sept. 1	Sept. 15
Ammonium Sulfate, export	100 lbs.	2.15	2.50
Blood, dried, f. o. b. N. Y.	unit	3.00	3.00
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	2.90 & .10	2.90 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.90	.90
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	2.25 & .10	2.25 & .10

*Resale or Imported (not an American Maker's price)

COAL-TAR CHEMICALS

		Sept. 1	Sept. 15
Crudes			
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U. S. P.	lb.	.18	.17
Cresylic Acid, 97–99%	gal.	.90	.80
Naphthalene, flake	lb.	.07	.07
Phenol, drums	lb.	.09	.08½
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.45	.45
Intermediates			
Acids:			
Anthranilic	lb.	1.30	1.30
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.30	1.30
Gamma	lb.	2.75	2.75
H	lb.	1.15	1.10
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.75	2.75
Naphthionic, crude	lb.	.70	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.27	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.18	18
For Red	lb.	.42	.42
Aniline Salt	lb	26	.26
Anthraquinone	lb.	1.75	1.75
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.50	.50
U. S. P.	lb.	1.50	1.50
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	5.00	5.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.45	.45
Dinitrobenzene	lb.	.25	.25
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.65
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.50	1.25
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.00	2.00
a-Naphthylamine	lb.	.35	.35
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.32	.32
m-Nitroaniline	lb.	.95	.95
p-Nitroaniline	lb.	.80	.80
Nitrobenzene, crude	lb.	.12	.12
Rectified (Oil Mirbane)	lb.	.13¾	.13¾
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.85	.85
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.70	1.70
Phthalic Anhydride	lb.	.40	.40
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	1.75	1.70
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.42	.42
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.45	.45
o-Toluidine	lb.	.25	.25
p-Toluidine	lb	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

		Sept. 1	Sept. 15
Acid Colors			
Black	lb.	.80	.80
Blue	lb.	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III	lb	.50	.50
Red	lb.	1.00	1.00
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb	.70	.70
Direct Colors			
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90
Sulfur Colors			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb	.85	.85
Chrome Black, domestic	lb.	.75	.75
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30
Basic Colors			
Auramine, O, domestic	lb.	2.25	2.25
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.70	70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	2.00	2.00
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	10.00	10.00
Victoria Blue, base, domestic	lb.	5.40	5.40
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of

INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society

Editor: CHAS. H. HERTY

Assistant Editor: LOIS W. WOODFORD

Advisory Board: H. E. BARNARD, J. W. BECKMAN, A. D. LITTLE, A. V. H. MORY, CHAS. L. REESE, GEO. D. ROSENGARTEN, T. B. WAGNER

EDITORIAL OFFICES:
One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613–0614

Cable Address: JIECHEM

ADVERTISING DEPARTMENT:
170 Metropolitan Tower
New York City
TELEPHONE: Gramercy 2145

Volume 13 NOVEMBER 1, 1921 No. 11

CONTENTS

EDITORIALS:

Danger Ahead . . . 974
Square Dealing . . . 974
A Nation's Loss . . . 974
Every Man's Job . . . 975
Notes . . . 975

FILTRATION SYMPOSIUM:

Washing and Washing Ports in Connection with "Chamber" and "Frame" Filter Presses. Eustace A. Alliott . . . 976
Filter Cloth and Its Relation to Filtration. Alvin A. Campbell . . . 982
Industrial Filter Media. Arthur Wright . . . 984
Fundamental Laws of Filtration with Suggestions Regarding Research Work. D. R. Sperry . . . 986
The Feeding of Filters. J. F. Springer . . . 986
Filter Aids. C. P. Derleth . . . 989
The Use of Filter-Cel for Industrial Filtration Processes. G. M. Hickey . . . 990
Centrifugal Filters. H. C. Beckman . . . 992
Discussion of Centrifugal Draining. T. A. Bryson . . . 993
Pulp or Filter Mass Filters. E. E. Finch . . . 996
Leaf and Rotary Suction Filters. G. D. Dickey . . . 997
Plate and Frame Filter Presses. E. C. Alford . . . 1000
Modern Leaf Type Filters. Robert C. Campbell . . . 1002
Oliver Continuous Filters. H. A. Morrison . . . 1005
The Atkins-Shriver Automatic Filter Press. H. D. Atkins . . . 1006
Vallez Rotary Filter. H. A. Vallez . . . 1007

EMULSIFICATION SYMPOSIUM:

Emulsions with Finely Divided Solids. T. R. Briggs . . . 1008
Emulsifying Agents in Oil-Field Emulsions. J. L. Sherrick . . . 1010
Common Characteristics of Crude Petroleum Emulsions. E. E. Ayres, Jr . . . 1011
Oil Field Practice in Handling Crude Oil Emulsion. Sidney Born . . . 1013
Recovering Petroleum from Emulsions by Chemical Treatment. Ralph R. Matthews and Philip A. Crosby 1015
Discussion on Electrical Dehydration of Crude Oil. W. G. and H. C. Eddy . . . 1016

ORIGINAL PAPERS:

The Removal of Free Acid from Nitrocellulose with Special Reference to the Use of Saline Leaches. S. E. Sheppard . . . 1017
The Production of Furfural by the Action of Superheated Water on Aqueous Corncob Extract. F. B. LaForge . . . 1024
The Color Value of a Tan Liquor as a Function of the Hydrogen-Ion Concentration. John Arthur Wilson and Erwin J. Kern . . . 1025
The Tannin Content of Pacific Coast Conifers. R. H. Clark and H. I. Andrews . . . 1026
The Alkaline Hydrolysis of Casein. Mary A. Griggs . . . 1027
Volume Increase of Compounded Rubber under Strain. Henry Green . . . 1029
Discussion of the Tetrabromide Method for Estimating Rubber Hydrocarbon. Harry L. Fisher, Harold Gray and Ruth Merling . . . 1031
Reactions of Accelerators during Vulcanization. III—Carbo-Sulfhydryl Accelerators and the Action of Zinc Oxide. C. W. Bedford and L. B. Sebrell . . . 1034
The Preparation and Instability of Tricalcium Arsenate. J. H. Reedy and I. L. Haag . . . 1038
Preparation of Mannose from Ivory-Nut Shavings. Paul M. Horton . . . 1040
Comparison of Results in Desugarization with the Steffen Lime, Barium, and Strontium Processes. Mich. Potvliet . . . 1041
The Effect of Varying Hydrogen-Ion Concentration upon the Decolorization of Cane Juice with Carbon. Joseph F. Brewster and William G. Raines, Jr . . . 1043
The Iodine Numbers of Unsaturated Hydrocarbons and Cracked Gasolines. W. F. Faragher, W. A. Gruse and F. H. Garner . . . 1044
Contribution to the Estimation of H-Acid. Henry R. Lee . . . 1049
Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis. G. L. Kelley and E. W. Evers . . . 1052
The Determination of Chromium in Ferrochromium by Electrometric Titration. G. L. Kelley and J. A. Wiley . . . 1053
The Use of Perchloric Acid as an Aid to Digestion in the Kjeldahl Nitrogen Determination. Brainerd Mears and Robert E. Hussey . . . 1054

LABORATORY AND PLANT:

Constant Temperature Rooms. E. G. Hastings . . . 1056
Flask Calibrating and Marking Device. Guilford L. Spencer . . . 1058

ADDRESSES AND CONTRIBUTED ARTICLES:

The Forests of the United States as a Source of Liquid Fuel Supply. Ralph C. Hawley . . . 1059
Colors Developed by Cobalt Oxides. H. J. Witteveen and E. F. Farnau . . . 1061

SOCIAL INDUSTRIAL RELATIONS:

A Method for Social Research. H. W. Jordan . . . 1066
Spare Time—A Defense . . . 1067
SCIENTIFIC SOCIETIES . . . 1068
NOTES AND CORRESPONDENCE . . . 1079
WASHINGTON LETTER . . . 1082
PARIS LETTER . . . 1083
LONDON LETTER . . . 1084
OBITUARY . . . 1085
PERSONAL NOTES . . . 1085
INDUSTRIAL NOTES . . . 1086
GOVERNMENT PUBLICATIONS . . . 1087
BOOK REVIEWS . . . 1091
NEW PUBLICATIONS . . . 1094
MARKET REPORT . . . 1095

Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.
Member of Audit Bureau of Circulations

EDITORIALS

Danger Ahead

For the successful removal of the causes of war by the conference soon to assemble in Washington, every good citizen will pray.

For the reduction of the present enormous expenditure of public funds for armament already more or less obsolete, every tax payer will hope.

However, in the matter of "control of new agencies of warfare"—wait a minute! In so far as this applies to chemical warfare there is something lacking in the make-up of the conference. We are not anxious about what our friends with whom we fought side by side are going to do with this new agency. The question becomes acute only when we think of that nation which initiated gas warfare, in spite of its plighted word, and whose chemical equipment, already strengthened by the demands of war, looms all the larger as other means of warfare are restricted.

It is an easy trap to walk into. Shall it be of our own setting?

Square Dealing

Why bother about strict editorial practice when your heart is full over good news bearing upon American chemical independence? Why speak in impersonal vein about men who are playing the game fairly and squarely and who are making history? If it be considered free advertising, then let it go at that, but we want every American chemist to know exactly what we learned in a conference in this office this afternoon.

The visitors were Mr. E. E. Kimble and Mr. Otis of the Kimble Glass Co., Vineland, N. J., and Mr. R. T. Will of the Will Corporation, Rochester, N. Y. From Mr. Kimble we learned a story of the attitude of union labor to the chemical glassware industry which is a veritable ray of bright sunshine, in contrast with the lowering clouds of the threatened railroad strike announced yesterday. At our request Mr. Kimble placed these facts in the form of a letter.

Dr. Charles H. Herty, October 17, 1921
1 Madison Ave.,
New York City.

My dear Dr. Herty:

In February, at the solicitation of the American Flint Glass Workers' Union, the Union met the Chemical Glass Manufacturers at the Hotel Walton, Philadelphia, and the Union volunteered to give a 15 per cent reduction in wages to meet the foreign competition with which they were confronted. A further voluntary reduction of 15 per cent was granted the manufacturers in August, 1921, in this same department.

The Chemical Glassware Blowers, an allied division of the Glass Workers' Union, accepted in August a voluntary reduction in wage of 17½ per cent, and increased the working move on many items, that is to say, increased the number of pieces per day, so that the reduction instead of being only 17½ per cent will come nearer to 25 per cent.

The action of these divisions of the American Glass Workers was highly commendable and to our mind shows the true American attitude, in that the glass worker has shown himself willing to help reduce the price of American-made glassware to come within reasonable competitive figures with imported ware.

Very truly yours,
(*Signed*) E. E. Kimble

That was fine—"But," we asked Mr. Kimble, "have you given the consumer the benefit of that lowering of cost?" "Every bit of it," he replied, "and for confirmation I refer you to Mr. Will." He in turn promptly confirmed the statement. Fine, again! "But, Mr. Will [the dealer], have you given the consumer the benefit of your cheaper purchases?" Quick as a flash, he turned to his printed prices in the 1921 issue of the "Chemical Catalog" lying nearby and showed us the new prices on standard chemical glassware and the prices of the same in his 1920 lists. Lowered, all along the line! To get the matter in more general form we immediately wrote Mr. C. G. Fisher of the Scientific Materials Co., Pittsburgh, Pa., and asked his current prices on the same items. Here are the prices resulting from the joint attitude of labor, the glass manufacturer, and the dealer.

	1920		Current Prices	
	Will Corporation	Scientific Materials Co.	Will Corporation	Scientific Materials Co.
Mohr's buret for pinch cock 50 cc. in 1/10	0.70	0.65	0.42	0.45
Liebig's condenser, sealed in coil 250 mm. length	2.70	2.05	1.30	1.15
Extraction apparatus, Soxhlet, 100-cc. capacity, ground joints	6.70	7.00	4.80	6.00
Volumetric flask, glass-stoppered with mark on neck graduated, 1000 cc.	1.25	1.40	0.93	1.20
Funnel, separatory, globe shape, stoppered long stem 500 cc.	2.65	2.10	1.75	1.65
Funnel tube, straight thistle top 250 mm.	0.11	0.11	0.10	0.10

That is the completed story. The lowering of labor's wages has been completely passed by the manufacturer and the dealer to the ultimate consumer, the chemist in the laboratory. It is a fine instance of square dealing.

During the recent Exposition we met Herman Coors of Golden, Colorado. "How about it, old man? What are you doing in chemical porcelain manufacture in these dull times?" "Never busier," he replied, "twice as many orders as in any previous year and doing business under the same motto." The reference was to a bit of advice we gave him several years ago—"Improve the quality of your goods every year, cut down the cost of production, be content with small earnings, and give the consumer the benefit of every possible lowering of costs."

These men, and others like them, have been able to stay in business because the greater number of American consumers have stood loyally by them, recognizing the difficulties of this trying post-war period and determined that in the future America shall be independent in such matters.

A Nation's Loss

Through the death of Senator Knox our chemical industries have lost a staunch friend. Representing particularly the great coke-producing region of Pennsylvania, he naturally became interested in the great economic loss which his state so long suffered through the failure to recover by-products in the coking industry. To avoid this loss he constantly supported every legislative aid for the development of our coal-tar chemical industry.

But Senator Knox was a statesman of wider vision than state lines. Watching closely the development of war methods, he quickly evaluated this industry as one of the most important factors in national defense. Therefore, when he saw the industry gravely threatened, through the approaching expiration of war legislation, he personally appeared before the Senate Finance Committee, eloquently urged an amendment to the Emergency Tariff Act to include synthetic organic chemicals, and succeeded.

Uniformly courteous, an intense student, a man of clear convictions backed by indomitable courage, a statesman from whatever angle viewed, his sudden death brought a sense of national calamity.

Every Man's Job

President Edgar F. Smith is in the saddle. Strongly impressed with the fine responses from the individual members of the SOCIETY to his request that each member communicate with his senators and congressman urging the necessity of adequate legislation for chemical industries, he now feels that the good work thus begun can be carried an important step further; namely, that individual chemists, each in his own neighborhood, must stir up public opinion about matters chemical. The carrying out of such a plan can be done best through the agency of the Local Sections. Therefore he has written to the chairman of each Local Section (and in the absence of his secretary on vacation each of these letters was written by his own hand, bless his heart) urging the appointment of a special committee to carry on an intensive campaign of popular presentation of chemistry in the territory of the Local Section. Again he has received a lot of fine responses, which he has forwarded to us to show the spirit prevailing among the leaders of our Local Sections.

Dr. Smith does not know of it, but in view of the numerous questions asked him in these letters, we are going to try to save him some correspondence by answering in a general way the points raised by some of the chairmen.

The work of the A. C. S. News Service is of course going ahead as usual. It may be of interest to all to know that while the maximum publicity, measured in inches of clippings received, at any previous General Meeting of the SOCIETY was 8000 inches, that of the New York Meeting is more than 30,000 inches, and the clippings are still coming in.

Invaluable aid has been given the News Service by the work of the Publicity Committees in many of the Local Sections, through their personal efforts in inducing the local press to make use of the material sent out by the Service.

The point Dr. Smith is driving at, however, is that the time has come when a larger and broader work must be done than the News Service can ever hope to accomplish. That the simple story of chemistry and its accomplishments is a fascinating one to our fellow citizens has been abundantly proved by the numerous addresses recently made by men in all sections before various groups of people. No oratory is required; the message will go across when backed by enthusiastic conviction on the part of the speaker that our chemists through their work are trying to serve this country and that this service can be best rendered only in an atmosphere of sympathetic public support. It has been inspiring to know how many men within the last two months have made distinct hits with such addresses. We are confident that six months ago these very men would have protested that they had no ability in this line.

There are numerous Chambers of Commerce, Boards of Trade, Kiwanis Clubs, Rotary Clubs, Women's Clubs, organizations of all kinds in all walks of life, who would gladly hear this story and, we are confident, would manifest that same enthusiasm which has characterized similar gatherings already addressed. Now any chemist would feel a hesitancy, through natural modesty, in requesting the privilege of addressing any of these bodies, but a live local committee could pick out of the membership of the Local Section a number of qualified speakers, and this committee could readily confer with the officials of these organizations and find a place on their programs for a local speaker.

Now is the time when such work must be done and can be done most effectively. We are not seeking to push the chemist forward, but we do wish this country to get the greatest possible good that can be gained from the work of the chemist. The battle which is on to-day is no figment of the imagination. It must be won. We would like to publish in these columns from month to month, if the local committees would give us the information, a list of the men who join in this good work, together with the names of the organizations addressed.

Don't depend on Dr. Smith, Dr. Little, and a few others to do the talking. It's every man's job.

Notes

Again the outbreak against industrial alcohol has shown itself in Congress: a proposal to put a tax which will amount to practically $12.16 on each ordinary gallon of alcohol, with a proviso that a return of the excess tax will be made when satisfactory proof is given that the alcohol has been used for industrial purposes. The proposal will scarcely become law, for its proponent did not seem to realize that many chemical firms would be called upon to invest more than their capital stock in deposits, and it would probably mean the tying up of more than $160,000,000 of the entire capital of the chemical industry.

Many chemists have to travel. It would be a pleasure to them to attend meetings of Local Sections while on such journeys, if they knew when meetings were to be held. Full calendars of the New York and Rochester Sections, the only two we have been able to secure, are printed in this issue (p. 1079). If secretaries will forward to this office, within the next ten days, dates of all meetings to be held this winter and next spring, a complete announcement will be published in the December issue for the information of our travelers.

The Emergency Tariff Bill, which includes protection for the synthetic organic chemical industry, is due to expire on November 27. A bill to extend this time to February 1, 1922, has been introduced in the House of Representatives, recommended favorably by the Ways and Means Committee, passed by the House, and is now before the Senate Finance Committee. It seems to be generally conceded that the bill will pass the Senate. Congress is plainly in no mood to let down the bars before permanent tariff legislation has been enacted.

The terrible loss of life and subsequent suffering resulting from the explosion of the nitrogen fixation plant at Oppau rouses nothing but feelings of deepest sympathy. It is to be regretted, however, that in his published interview on the subject of the explosion, Professor Haber has made use of the occasion to try to place upon the French the responsibility for the introduction of gas warfare. The world understands this question too well to be misled by any such piffle.

It has been gratifying to learn that the resignation of Hon. Thomas W. Page as Chairman of the United States Tariff Commission has not been accepted and that he will continue to serve in this capacity. Under his guidance the Commission, as an agency for collecting reliable data on which to base legislation, has gained steadily in public confidence.

If there be those who do not understand the meaning of the resolution of the Council regarding the report of its Patent Committee (page 865, October issue), let them read the eye-opening story about the influences which shaped some of our present patent legislation, as set forth in the address of Hon. Francis P. Garvan before the recent General Meeting of the SOCIETY, printed on page 867 of the same issue.

FILTRATION SYMPOSIUM

Papers presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

Washing and Washing Ports in Connection with "Chamber" and "Frame" Filter Presses

By **Eustace A. Alliott**

Manlove, Alliott & Co. Ltd., 51 & 42 Parliament St., Westminster, London, England

Washing in the filter press is resorted to either (*a*) to recover a valuable liquor from the solid particles which retain it, or (*b*) to free such particles from impurities dissolved in the adhering liquor. Both requirements may of course be combined in one particular instance. In the first case it is usually desirable to avoid dilution, and while this may not be so important in the second case, there is little doubt that methods which involve the formation of much weak liquor tend to allow some portions of material to receive comparatively little washing, and promote inefficiency. The ideal in all cases therefore is to use the minimum of wash which will give the results required, for which the primary conditions are that the cake itself should be uniform and in the proper physical condition, and that every section shall be washed at an equal rate. It is proposed in the present paper to consider: (1) some of the physical factors which affect washing, (2) the various mechanical appliances for effecting it, and (3) some practical and experimental results.

PHYSICAL FACTORS AFFECTING WASHING

The flow of wash through a filter cake certainly appears, as an experimental fact, to approximate in many cases to the rules which hold for capillary passages.[1] The flow is inversely as the cake thickness, and very nearly proportional to the pressure. This proportionality is very liable to be disturbed by the fact that the filter particles may become distorted or crushed under pressure, thus decreasing the area of the capillary passages, while the physical condition of the cake may change during washing. It is more difficult to show that the flow varies inversely as the fourth power of the passage diameter, and it must not be forgotten that these passages are not straight as required by the theoretical formula, but are very sinuous. Nevertheless, it is a matter of observation that the rate of flow diminishes sensibly and very rapidly with decreased size of capillary pores, and also in proportion to the viscosity.

Nominally, washing consists of a displacement of mother liquor from the pores between the particles by an equal volume of wash, in which process little or no mixing of wash andliqu or takes place. Such perfection is, however, rarely obtainable, even in theory, as various disturbing factors occur, of which the following are the most important:

1—Adsorption
2—Capillary diffusion
3—Formation of chemical compounds
4—Colloid formation on removal of electrolytes

ADSORPTION—Adsorption is the unequal distribution of the solubles at the boundary between the solid and liquid phases of the cake owing to surface energy effects, and in many cases a large excess of solubles is thus retained in the surface film and does not pass away with the displaced liquor. This occurs only when the solubles in question tend to reduce the surface energy, and the amount retained is in equilibrium with the strength of the surrounding liquor in the manner shown by the equation

$$\frac{S}{W} = KC^n$$

where S is the weight of the soluble matter adsorbed by W, the weight of adsorbent, C is the volume concentration of the surrounding wash after adsorption is complete, and K and *n* are constants, *n* being less than unity. The effect is proportional to the area of the boundary surface, and is thus of most importance in fine-structured or gelatinous precipitates, and where the cake particles are highly porous. Its general tendency is to multiply the proportion of wash required, since the amount of solubles retained decreases as a rule a good deal more slowly than the dilution of the washings. As the latter pass through the cake they displace the liquor loosely retained between the particles, but leave on the surface at each point of the cake an amount of adsorbed solubles in equilibrium with the strength of washings at that point. A pair of curves could therefore be drawn for the concentrations of adsorbed matter and wash for each succeeding layer, rising from zero at the inlet face to values at the outlet face dependent on the amount of wash and the cake thickness.

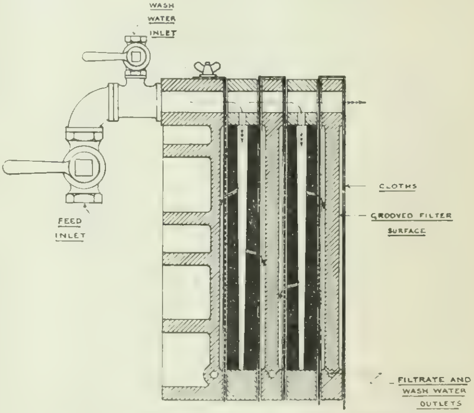


Fig. 1—Simple Washing in Plate and Frame Filter Press

In order to understand the effect of the latter factor, let us consider any thin section of the cake. It will be apparent that the strength of the wash tailings will have fallen well below the original equilibrium concentration, *i. e.*, the strength of the original mother liquor before the adsorbed solubles are appreciably reduced. Hence they can be further employed to remove a portion of impurity from a succeeding layer, which therefore will not require so great an appropriation of additional wash as if it had been treated separately. The tailings from this can again remove a portion from a third layer, and so forth, each succeeding layer requiring a somewhat smaller addition to the total amount of wash. It will be clear that a thick cake will require less wash than a thin one, but the advantage, though considerable for the first increases in thickness, does not increase at the same rate if further thickness is added; and it must be remembered that very thick cakes are not always practicable because the rate of flow is seriously diminished unless they are reasonably permeable. The washings, however, may be graded

---

[1] The flux in a capillary tube is given by $F = \frac{\pi a^4}{8V}\left(\frac{P_1 - P_2}{L}\right)$, where P_1 and P_2 are the pressure heads at either end, a is the radius of the passage, L is its length, and V is the viscosity of the liquid at the particular temperature.

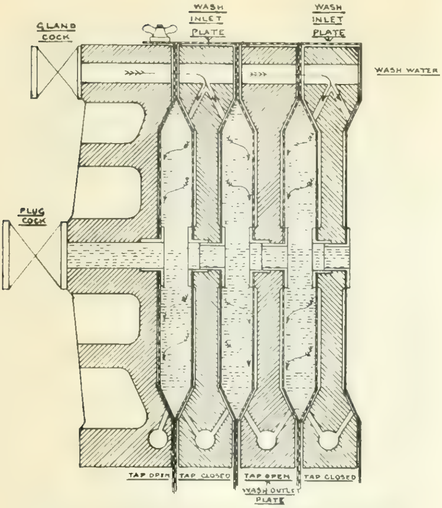


FIG. 2—THOROUGH WASHING IN RECESSED PLATE PRESS

and used in succession, beginning with a strength not too far removed from that of the original strong liquor, following this by a weaker one, and finishing with a small portion of pure wash. The introduction of weak liquor into a process may thus be reduced to minimum, even if adsorption effects are great.

CAPILLARY DIFFUSION—Absorption of mother liquor by capillary diffusion into the pores of the cake particles may take place. In this case, the washings have to be dilute before its effectual removal begins, and a time factor, which may be considerable, also comes into play. In the case of, say, iodine solution and charcoal, weeks may be required before an equilibrium is established. The effects are similar to, if more complex than, those of adsorption, involving an additional proportion of wash and a longer time.

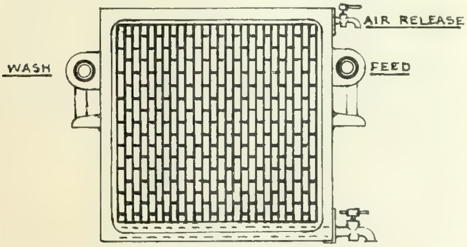


FIG 3—PLATE WITH FEED AND WASH CHANNEL IN OUTSIDE LUGS AND HAVING RUBBER JOINT RINGS

CHEMICAL COMBINATION—Further, the solubles may be retained by chemical combination with the substance of the filter particles, such compounds being stable only when the concentration of the liquid phase is in excess of a certain critical amount. None of the solubles will then be removed till the washings become diluted to this critical concentration, which will be maintained till all the unstable compounds have come away. Such cases often occur in fine chemical manufacture and are especially to be observed where organic bases are isolated as picrates. The excess of wash required varies directly as the quantity of solubles retained, and inversely as the critical concentration.

COLLOID FORMATION—Many precipitates are held in the coagulated state only in the presence of suitable electrolytes, and revert to a finer structure or even disappear when these are removed. Hence, when wash enters a cake of such a nature and removes the electrolytes, the inlet face of the cake becomes highly gelatinous and impermeable. If the wash does succeed in penetrating deeper layers it meets a higher percentage of adsorbed electrolyte, and its content of electrolyte increases until enough accumulates to cause coagulation to occur again, choking the pores of the cake and rendering it still more impermeable. If washing is persisted in, a further decoagulation is obtained, and the cycle is repeated until the precipitate finally passes out of the press through the cloths. Here stage treatment with washes of graded strength has a peculiar advantage, as the entering wash always contains a little electrolyte, which is not completely withdrawn from the first layers till the bulk has been removed from the later ones, and the latter may therefore be washed well without decoagulation occurring. Thus it is often possible to obtain purer cakes than by any other method, with reasonable consumption of wash and time.

CONTROL OF QUALITY

SIZE OF GRAIN—It will be clear that precipitates should not be of too fine a grain, in order that trouble due to surface action may be avoided, and that the cake pores may be sufficiently large to allow a reasonable flow. As a rough guide, 2μ may be taken as a limiting size of grain, above which washing is usually comparatively easy, and below which troublesome conditions begin. In this connection it must not be overlooked that small, precipitated grains are more soluble than large ones, and it is often possible to control the quality of a precipitate by prolonged digestion in contact with mother liquor. The small grains tend to disappear, and the larger ones to increase. The user has a valuable means of control ready to his hand, which is often overlooked, but which may have more bearing on good results than the most perfect mechanical appliance. The varying degree of attention given to this point renders almost impossible any close comparison of results obtained in various works with different types of plant.

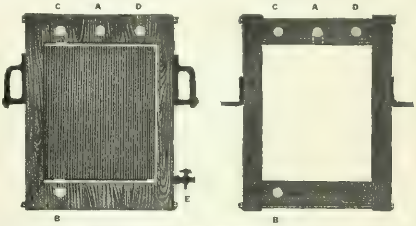


FIG. 4: A—FEED INLET; B—WASH WATER INLET; C—AIR OUTLET (C SHOULD BE CLOSED AS SOON AS WASH WATER APPEARS); D—WASH WATER OUTLET; E—OUTLET FOR FILTRATE (WHEN WASHING ALL THE OUTLET COCKS E SHOULD BE CLOSED)

In extracting soluble matters from ores and earths fine grinding is usually advantageous, as it permits the free escape of the solubles, which should be brought into solution before the liquor is pumped to the press. It is still desirable not to form more very fine slime than can be avoided, and prolonged boiling is helpful in bringing the particles into the best condition for filtration and washing.

TEMPERATURE—It must not be overlooked that increased temperatures are always desirable where permissible, as viscosity is generally very appreciably reduced by their use, permitting a more rapid flow, while adsorption is usually decreased.

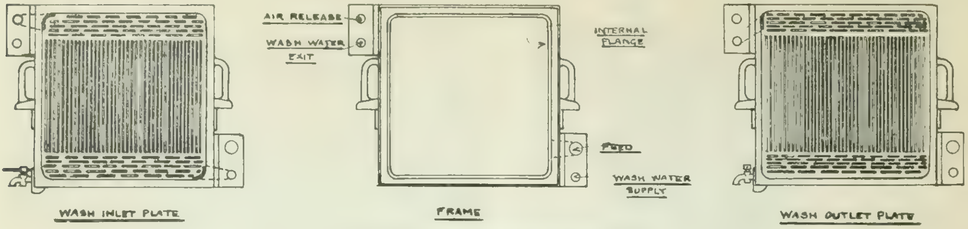


Fig. 5—Thorough Washing with External Lug

Methods of Washing

We now come to the question of the manner in which the wash is best applied to the filter cake. The various mechanical disturbances that are liable to occur will be dealt with at the same time.

SIMPLE WASHING—The simplest method, known as "simple washing" (Fig. 1), is to use the feed passage for the admission of the wash water. For the best results the cake should not be fully formed, but left incomplete with a hollow center, into which the wash passes, driving out the unfiltered liquor and itself passing through each face of the cake. Various users report that they are able to get satisfactory results even if the cake is solid, but it is clear that, in this case, there are possibilities of uneven results, as there will be very appreciable resistance to wash passing any distance through the solid cake, and it will escape more readily near to the point of admission. Where the cake is not fully formed the wash has free access to every part, and there is also an automatic tendency during filtration to equalize the resistance of all portions of the cake. While there is such a tendency, it does not, however, necessarily follow that it can work out fully unless conditions are favorable, and as soon as the two halves of the cake touch at any point, it ceases to exist.

Unfortunately, there are disadvantages connected with this method of washing. Care has to be taken that just the right amount of liquor of correct strength is pumped into the press, and space and press capacity are of course wasted and more labor is required for emptying out than if a firm cake were to be formed. This method is therefore usually reserved for materials which form a solid cake with difficulty. It also is a useful stand-by if it becomes necessary to wash when no specially constructed presses are available. The position of the feed passage affects this method very little, but a bottom feed permits the remaining strong liquor to be removed from the press before admitting the wash, which otherwise would dilute it, and the chambers can also be thoroughly drained before opening the press. This may, however, be done by compressed air, if available, while with materials tending to settle rapidly the port from a bottom feed might become silted up.

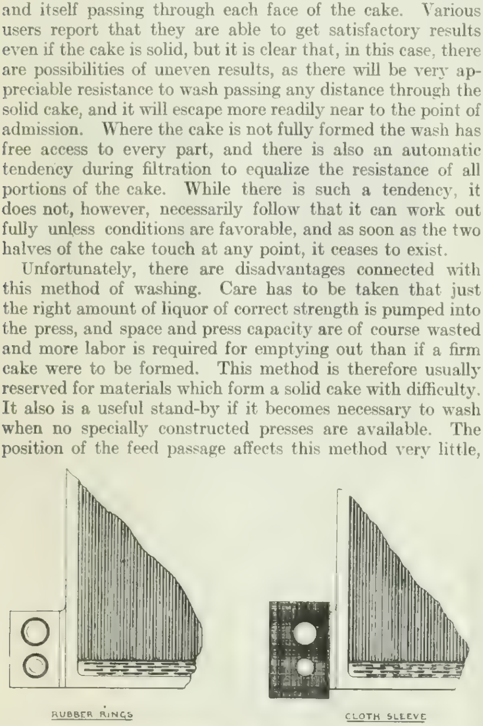


Fig. 6—Methods of Making Joints on External Flanges

THOROUGH WASHING—Another method is to force the wash right through the cake from one face to the other, and this may be referred to as "thorough washing" (Fig. 2). In its simplest form there is a wash-admission passage in the rim of the press, with ports connecting it to the business surface of each alternate plate. Before commencing to wash, the taps on the wash inlet plates are closed, while those on the intermediates are left open. The wash must now pass through the cake and cloths to the intermediate plates, where it escapes through the taps. It will be seen that in this case a fully formed cake is necessary.

A serious defect in this method, which is largely in use on old pattern presses and is now becoming obsolete, is that air is likely to be trapped in the filter surface, or may leak back through the taps at the close of filtration. This cannot always escape readily through the joints, especially as wash pressures are not always high. Thus the wash is prevented from penetrating the upper portion of the cake. One way of avoiding this difficulty is to provide an air outlet tap at the top of each chamber. This is done in some modern presses (Fig. 3).

There is, however, still a defect, which in some cases will lead to unequal washing: namely, the wash can run straight out of the taps after it has passed through the cake and does not necessarily form a wall of water behind the latter similar to that on the inlet side. This means that at the bottom of the cake there is an unbalanced hydrostatic pressure which may lead to an undue amount of wash passing through at this point. When it is understood that in some instances the total head desirable for washing may amount to only a very few feet of water it will be seen that this may be a serious factor. It is further to be borne in mind that although recessed plates entail less labor than plates and frames, they are inferior to the latter for washing purposes, inasmuch as the edge of the cake is necessarily thinner than the remainder, allowing a greater flow of wash, which entails mixed washing. Further, in recessed plates, the feed channel is necessarily inside the rim, and in nearly all cases the feed is internal to the cake itself. There is no special reason why the wash should pass through this core of material in the feed passage if it is solid, while if it is soft an opportunity may offer for short-circuiting. How can all these factors be taken care of? For the best results it would appear necessary to secure the following conditions:

1—The press should be of the plate and frame type.
2—Means should be provided for air elimination.
3—The wash must leave at the top of the press, so that the cakes are immersed in a bath of wash eliminating any unbalanced hydrostatic head.

Presses in which all these conditions are observed may be referred to as of the "thorough washing" type.

In a common form, the wash inlet passage is arranged inside the rim of the press at the bottom corner and the top corners are occupied by the air and wash outlet passages, respectively. The wash first passes through connecting ports to the filter surfaces of alternate plates rising behind

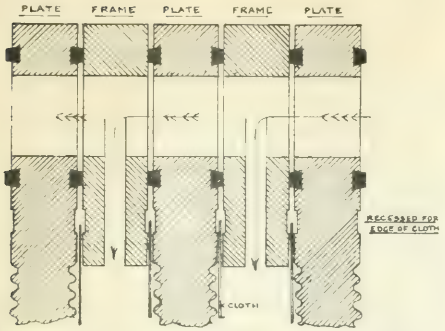


Fig 7 Section Showing How Rubber Rings Are Inserted. Method of Making Joints on External Flanges

the cloths and driving out any air into the air passage, which is connected by ports to the wash inlet plates only. As soon as water overflows from the outlet cock of the air passage, the latter is closed, and the wash must then pass to the intermediate plates, where it rises and overflows into a wash outlet passage which also provides a means of escape for any trapped air from the intermediate plates. Fig. 4 shows this method applied to wood plates and frames. All the holes, but one, are at the top of the plate, which avoids difficulties due to shrinkage and simplifies adjustment of the cloth.

In an alternative method of construction, the holes are all in one side piece of the wood plate, which facilitates and cheapens repairs and renewals.

In cast-iron presses, in cases where the cloths have to be frequently changed, it is worth while to go to the additional expense of having the passage formed in external ears in the manner shown in Fig. 5. The joints on the ears or external lugs are made by means of cloth sleeves (Fig. 6), which are provided with the necessary holes corresponding to the various passages. The main cloth covering the face of the plate is thus quite plain and may be speedily taken off and replaced, as there is no need to adjust it with regard to the various passages, as is the case in the type formerly mentioned. Further, if shrinkage of the cloth occurs, it is not of any consequence. Against these advantages there is of course the additional expense of the cloth sleeves, and the plates themselves are more costly to manufacture. It is therefore not usually worth while to instal this particular type unless cloth renewals are likely to be fairly frequent.

The cuffs or sleeves will want renewing from time to time; but if care is taken in cleaning out the ports, a sleeve may outlast several cloths. A case came to the author's notice where the sleeves on the air and wash outlets averaged twelve months' life, as against three months for the cloths. The sleeves on the feed ports did not last quite so well on account of the additional cleaning required. Where rubber joints are permissible, they may be used instead of the cloth sleeves. One method (Figs. 6 and 7) is to fit rubber rings into grooves in the lugs, which are made with slightly tapered sides, while an alternative practice is to make the passages themselves rather larger, and to fit in rubber rings which project slightly on either side. Such rings are as a rule made with a slight lip on the interior at each end, as this tends to make a better joint under pressure, but quite good joints can, as a rule, be made even with plain rings. This loose type of ring is more readily renewed, but the others are better from the point of view of ease in cleaning the passages. The rings are of course fitted to lugs which have no connecting port to the plate or frame.

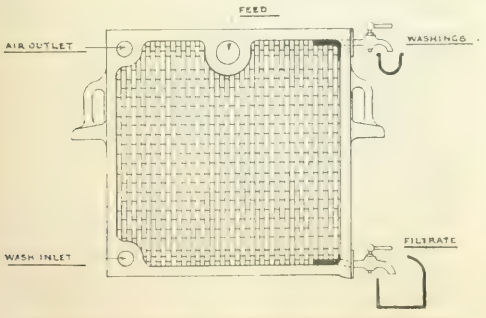


Fig. 8—Washing Press with Special Taps for Wash Outlets

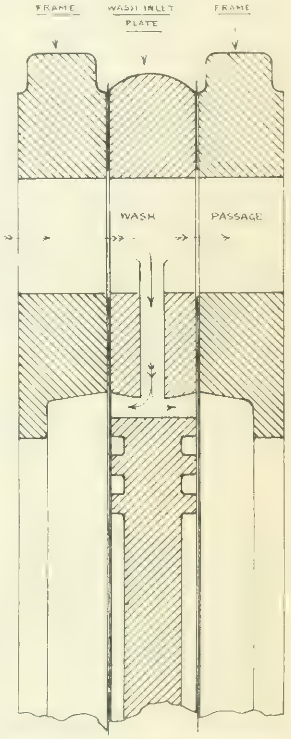


Fig 9 Diagram Showing Arrangement of Flanged Frames, Preventing Leakage of Wash Round Edges of Cake

In the above instances of thorough washing arrangements the wash leaves by an enclosed outlet. Should it be desired to control the washings from each separate chamber, wash outlet taps may be fitted at the top of the plates, delivering into a special light gutter (Fig. 8), which can be lifted away when it is desired to clean out the press; but while this is perhaps the most perfect arrangement possible from the point of view of the control of washing, more labor and attention are involved and the enclosed outlet type is more usually adopted. It is interesting to note some of the possibilities of these thorough washing presses with enclosed wash outlet. There are a dozen or more ways in which the passages can be used. For instance, it is perfectly feasible to subject the cakes to a reverse wash by using the ordinary wash outlet as inlet passage, and the filtrate taps or the air passage as outlet; and the cloths may be cleaned by subjecting them to a reverse flow of water, air, or steam when the press is empty. The press can also be used without alteration if it is desired to take the filtrate through enclosed outlets instead of through the taps. The only requisite for these various uses is that the necessary piping connections be made to the fast head.

A fruitful source of unsatisfactory washing is leakage around the edge of the cakes. The slightest shrinkage of the cake will give rise to this, but it may be of serious consequence in cases where shrinkage is not at all apparent.

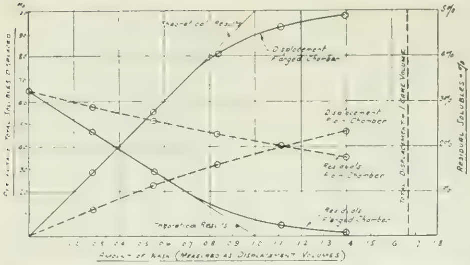


Fig 10 Comparative Washing Results for Flanged and Unflanged Frames for Spent Oxide Cake 2 In. Thick

Practical and Experimental Observations

LOCATION OF LEAKAGE—Mr. H. E. Williams, faced with the difficulty of dealing with a large volume of weak liquor from filter-press washing, carried out some investigations on this problem. A highly colored solution was used as the wash, and it was clearly demonstrated that leakage was taking place at the junction of the edges of the cake with the internal edges of the frame. Since the plane of this junction was parallel to the direction of the wash pressure, there was no possibility of forming an effective seal.

The problem was finally solved by making an internal flange or rabbet on the wash outlet side of the frame (Fig. 9). Several filter presses fitted with this special type of frame were in use for some time in the extraction of prussiates from spent oxide, and comparative figures were obtained on a works scale from chambers fitted with both the flanged and unflanged type of frame.

The material was ground with weak liquor, limed and filtered at 60 lbs. per sq. in., and containing about 34 to 36 per cent of liquor. This was washed with water at 80 lbs. per sq. in. The pressure of the wash, which should be applied as rapidly as possible, forced the cake against the flange or rabbet on the wash outlet side of the frame, forming a very efficient seal and completely preventing any leakage round the edges of the cake.

Each cake was 2 in. thick, and the retained liquor contained 9.2 g. of prussiate of soda per 100 cc. In Fig. 10 the actual displacement of solid matter is plotted against the volume of wash liquor, and demonstrates very forcibly the advantage gained by the use of flange. The percentage of soluble matter left in the cake is also shown for both cases.

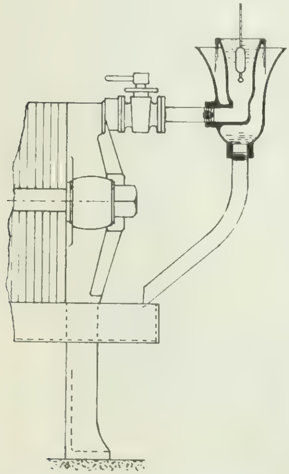


Fig. 11—Diagram of Hydrometer Attachment on Wash Water Outlet

The average strength of the washings was 6.6 g. of prussiate of soda per 100 cc. for the complete washing with the flanged chamber, but for the unflanged chamber the strength was only 3.2 g. per 100 cc., while less than half the soluble matter had been removed.

It was found that several years ago a patent had been taken out for a very similar device, which apparently has not received the recognition it deserved. It is surprising that it has not been generally adopted, as the slight extra labor involved in the cleaning may be very amply compensated by the increased strength of the washings.

The author's own experiments confirm the fact that leakage may exist at the cake edges even in the case of so easily washable a cake as spent lime. In tests on 2-in. cakes with colored washes the edges were stained through, and color issued before the cake was half penetrated in the center.

It should be borne in mind that cakes which go moist when shaken in the hand are specially liable to shrinkage through any slight disturbance, and are then more prone than ever to allow wash to short-circuit at their edges. This is due to the fact that when the particles of the cake consist of hard grains which are actually in contact, the most compact formation is not assumed in the first instance, and rearrangement is likely to occur.

TESTING STRENGTH OF WASHINGS—To obtain the best results it is well not to rely on washing for a given period, or putting a given amount of liquor through the press. Regular tests should be made of the strength of the washings, and the process should be stopped as soon as these fall off. For this purpose it is well to have a hydrometer bowl (Fig. 11) fitted to the press head, so that readings may be taken continuously as the washings issue. It is also a convenience to fit a thermometer, and where the gravity of the washings is not a reliable guide, it is often possible to devise a simple chemical test which can be applied even by an unskilled operator.

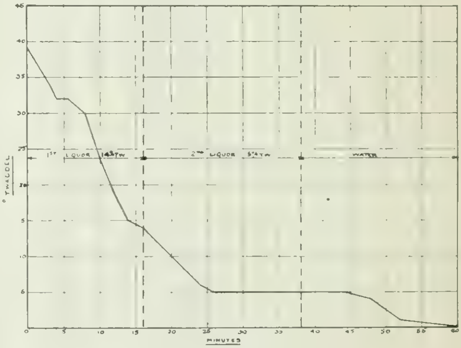


Fig. 12—Washing Carbonate of Lime Filter Cake (Contaminated with Colloidal Silica)

SELECTION OF CLOTHS—The rate and efficiency of washing is affected by the cloth. The essential point is that the cloth shall not be finer than is requisite to give a clear filtrate after a small amount of liquor has been pumped through. If this precaution is observed the cloths will clog far less readily and will not require renewal so often. If fine cloths are requisite they should be of light weight and supported on strong backings of open weave.

PRESSURE APPLIED—Probably the conditions under which the cakes are made have as much influence on good washing as any other factor. If the cake is incorrectly formed the most perfect mechanical arrangement will not give satisfaction. The first point is the pressure at which the cake is finished off, which should be high enough (except in the case of simple washing) to give a firm and complete cake.

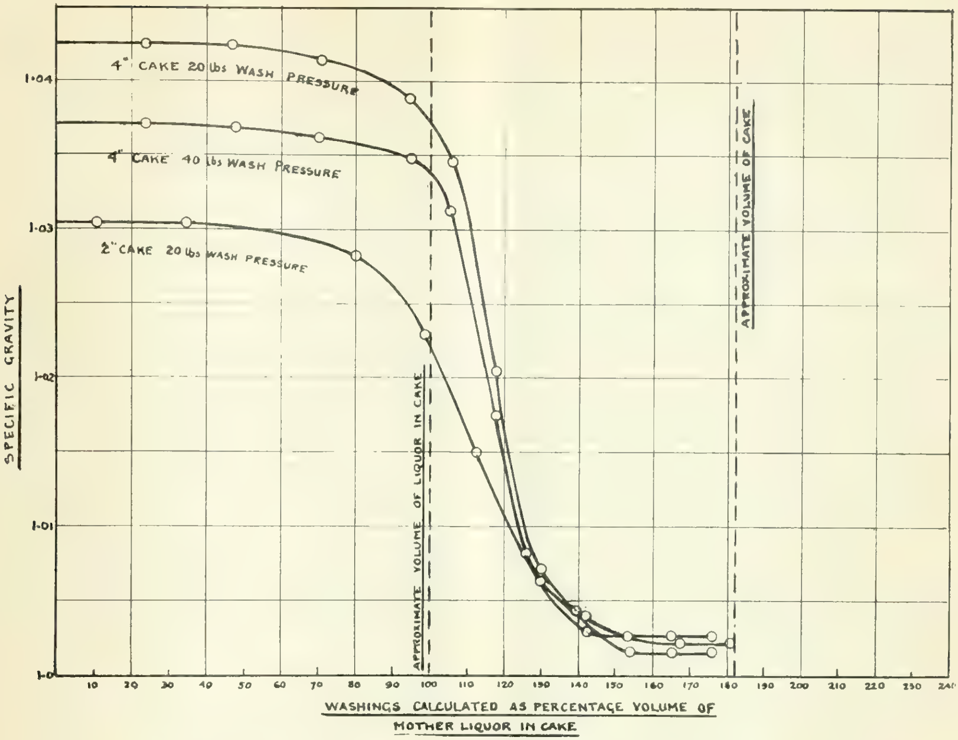


Fig. 13—Washing Weak Caustic Soda Solutions from Carbonate of Lime Cake (Experimental)

Excessive feed pressure, however, may render the cake unduly impermeable, especially if it is inclined to be gelatinous, while channeling of the cake and short-circuiting is very liable to occur. Further, a time element is necessary to allow for diffusion of the solubles out of the interior of the particles if these are porous, and this is not necessarily reduced by a rapid flow. In an instance of washing tin slimes containing wolfram, where the cake had been consolidated at 80 lbs. per sq. in., the best results were obtained with a wash pressure of only 4-ft. head of water. While high pressures are requisite in some cases, washing should be carried out, in general, slowly and at the lowest practical pressure.

FEEDING OF FILTER—Often the buyer objects to paying for a suitably large pump, so that this portion of the plant is usually cut down to its finest limits. Although this minimizes pumping of the liquor through the relief valve in the later stages of the pressing operation, time is given for selective settling in the press, resulting in the larger particles being in excess at the bottom of the cake and the finer ones at the top. This gives rise to varying permeabilities, washing does not proceed on a parallel front, and unsatisfactory results occur. A similar effect is very likely to result through any stoppage or disturbance in the pumping, due to a broken belt, change of shift, or other reason. It is therefore essential for good washing that the cake shall be formed at maximum rapidity with a steady and regular flow. The coarser particles are then uniformly distributed among the more slimy ones and perform their proper function of keeping the whole cake more open and porous. There is no doubt that from this point of view by far the more satisfactory results are obtained by feeding by means of compressed air, using a monte-jus or sludge ram, which it may occasionally be desirable to fit with an agitator. The ram should be of a suitable size to charge the press in one operation, but if the volume of liquor is too great it is an advantage to have a second ready to start feeding as soon as the first is empty. As a result of the perfectly steady feed pressure, the cake itself is likely to be more open and permeable than that obtained with a reciprocating pump, even though the latter were of suitable size. The pulsations, especially of a single-acting pump, tend to disturb the particles in the cake, assist them to settle into their most compact and least permeable structure, and may also cause them to clog the cloth, so that the penetration of the wash is made difficult. If plunger pumps are used they should have an air vessel of very ample size. It should be noted, however, that a compressed air feed will give the very high rate of flow it is often possible to obtain when the press is first being started up, even at comparatively low pressures, without the use of any relief valve or other troublesome working part, since the larger volume of the air at lower pressures compensates for the extra duty. In one instance which came to the writer's notice, in washing a cake of rather sandy nature in which some slime was present, it proved impossible to attain a lower limit than 2 per cent of soluble matter, no matter how much time was taken or how great a quantity of wash was put through. When the small plunger pattern feed pump in use was replaced by a monte-jus fitted with a suitable agitator, no difficulty was experienced in washing to 0.2 per cent within quite a reasonable period. It should be realized that, in "through" or "thorough" washing, the wash has to pass through the whole thickness of the cake, instead of only half, as in the case of the filtrate, and for this reason, the cakes, unless readily permeable, should be thinner when washing is involved than if filtration only is requisite.

EFFECT OF NATURE OF PRECIPITATE ON TIME OF WASHING—If the particles in suspension are of a hard and nonporous character and are confined within reasonable limits of size in either direction, washing becomes an easy problem. The theoretical curve connecting concentration and amount of wash will be a horizontal line, dropping sharply to zero as soon as an amount equivalent to the volume of liquor in the cake has been forced in. The effect of adsorption, etc., is to cause this curve to drop less and less sharply the finer the grain of the cake, as the specific surface of the grains increases with decrease in grain size. Fig. 12 shows some experimental curves obtained by the author. A weak caustic solution was filtered from a chalk precipitate; the cakes weighed about 92 lbs. per cu. ft., contained 38 per cent of moisture, and were formed at 80 lbs. per sq. in., using a monte-jus. They were washed at 20 lbs. and 40 lbs. per sq. in., and displacement was nearly perfect. Almost theoretical results were obtained as the cake was quickly formed and of even quality throughout. Washing was complete with about 1.5 to 1.8 displacement volumes or, say, 0.84 to 1 cake-volume of wash. This result was due to the fact that the pressure was not high enough to cause appreciable leakage round the edges of the cake. In similar experiments, in which the cake was formed and washed by a hand-pump, using 100 lbs. pressure in each case, several times the amount of wash and a longer period of time were requisite unless great care was taken.[1] These results were very fairly indicative of what could be obtained on a large scale. In ordinary commercial practice a press was used making cakes 1.75 in. thick, which were formed at 80 lbs. pressure and washed at 15 lbs. pressure. The time required for washing with hot water was 10 min., the rate of washing being 8.2 gal. per sq. ft. per hr., and the amount required being about 1.5 cake-volumes. The residual soluble matter was 0.18 per cent on the wet cake.

The case, however, is immediately altered if slimy matter is present. The following figures relate to a cake consisting of precipitate of lime contaminated with colloidal silica. Here the cakes were approximately 2 in. thick, weighed 93.5 lbs. per cu. ft., and were 51.5 per cent moist. One hour was required for washing, the rate of flow being 4 to 5 gal. per sq. ft. per hr. The amount of wash was 4.25 times the cake-volume or 5.5 displacement volumes. By washing in stages as shown in Fig. 13, using liquors of decreasing strengths, the amount of pure water required was reduced to approximately one-third of the total wash volume. The amount of residual soluble matter was 0.4 per cent, measured on the wet cake.

Mr. H. S. Denny has made very full investigations in connection with the filter pressing and washing of gold slimes.[2]

For many fine-grained or gelatinous precipitates much more time and wash are required. In washing chrome hydrate, 2.5 hrs. were necessary, for cakes 1.25 in. thick. The wash amounted to 10 cake-volumes, the cake weighing 80 lbs. per cu. ft., with a moisture content of 75 per cent. The rate of washing was 2.6 gal. per sq. ft. per hr. It is impossible, however, to give any general rule, as the circumstances vary very greatly for each substance. Similar conditions occur with many dyes and intermediates, and even longer wash periods may be necessary.

CONCENTRATION—Where the liquor contains solubles dissolved at a high temperature, care must be taken that the concentration is such that these are not precipitated in the press, owing to the cooling which may take place there. Unless such a precipitate dissolves very readily it will be very difficult to wash out, owing to the low turbulence of the wash water, and if any part is removed there will be a tendency for the cake to shrink, giving rise to irregular washing. In dealing with a certain dye intermediate, suspended in a liquor containing a proportion of sulfate of soda, satisfactory results were not obtained even after many hours' washing. It was found that the sulfate of soda was crystallizing out, owing to a slight drop in temperature between the vat and the press. On diluting the mixture in the vat just sufficiently to prevent this, good results were obtained in a perfectly normal wash period. It will be realized that washing in the filter press should be used only for removing matter already in solution. It is not a substitute for good lixiviation.

In conclusion it may be said that owing to the large number of factors which enter into a washing problem, it is not possible to lay down hard and fast rules and figures, and each problem must be considered in regard to its special circumstances. There is no doubt, however, that in too many cases the operation is carried out without regard to principles. A precipitate is taken as it happens to come, a cake is formed somehow, the wash applied anyhow, and finally those responsible complain that their material is difficult to handle, or that there is some defect in the design of their filter press.

It cannot be too clearly understood that good results depend not merely on the mechanical arrangement of the press, but almost more on the attention paid to securing a proper physical condition of the material to be treated, and delivering it in a suitable manner to the press. Every detail of the operation should be correct.

---

[1] It should be noted that all rates of washing are calculated on the half area only of the filter press.

[2] "Rand Metallurgical Practice and Recent Innovations," *Proc. South African Assoc. Eng.*, **11** (1905).

Filter Cloth and Its Relation to Filtration

By Alvin A. Campbell

Newark Wire Cloth Co., Newark, N. J.

Under the heading of filter cloths we may select a few of the leading ones, woven of cotton, wool, jute, hemp, nickel, and monel metal.

Cotton duck has been used for years for practically all filtering media up to the present day, wherein we look for something to replace cotton; not so much with the view of giving a better separation as of an increased efficiency, figured down to output versus cost.

After all, the filter cloth does not do the filtering, but acts as the retaining wall to form the cake. With this fact in mind we have but one principle to follow: that is, to combine strength, fineness, and rapidity.

Strength, Fineness, and Rapidity

First, we require strength in the medium in order to withstand the pressure applied through the pumping of the liquids through the press. One great cause of leakage in most plate and frame presses is that the cloth, when under pressure, finds its way into the fissures or grids of the plates, and in patented types of presses into the meshes of the heavy wire cloth backings of the plates. This causes a distortion of the meshes of the vegetable and animal fibers used in the manufacture of filter cloths, which in turn causes larger openings and a leakage. The answer to this point is change of design in the weave.

Secondly, we may combine fineness with rapidity. It can be readily understood that the finer the cloth, the less the rapidity. To change these conditions means change of design, not only in the weave but in the material from which the cloth is fabricated.

Effect of Materials to Be Filtered

In the chemical field we find a great variety of substances to be filtered, such as those of viscous character, alkalies, acids, and saccharates, and in the manufacturing field we are confronted with different industrial problems. Perhaps the greatest problem, outside of the strictly chemical field, is that of the clay industry. In considering all these problems we must watch for a chemical action on our filtering medium.

While we know that cotton duck, for instance, will produce the desired results as far as filtration is concerned, we must constantly renew our cloths because of the effect of the substances passing through. We know that both alkaline and acid conditions will bring about decomposition of cotton, thereby causing a decreasing efficiency of the cloth, and finally a complete change of filtering media. It is therefore desirable to find a material from which to make filtration media, which will withstand the action of chemicals.

Any of the cloths made up of the vegetable or animal threads are not entirely satisfactory from the point of view of rapidity of filtration and the filtration pressure developed by the pressure applied to the press in pumping the liquids through. When the cloth becomes wet a swelling and softening of the fiber takes place, permitting the cloth to become distorted. Larger openings and a less efficient filtration result, especially when additional pressure is placed upon the pumps to speed up the process.

Metallic Cloths

A metallic medium seems to promise most, and monel metal seems to be the logical metal to be used. This is indicated by experimental data on the resistance of monel to various acids and salts, and it is a known fact that it is alkali proof.

In the use of monel metal filter cloths we must, however, guard against one thing, the electrolytic action set up when using it in connection with iron plates. While there may be other substances which will attack monel metal filter cloth, potassium permanganate is the only one which sets up a violent electrolytic action which has come to the attention of the writer. There are, of course, other materials which cause electrolytic action, but none are on record where the value of the cloth is impaired.

Monel metal cloth is about twelve times as strong as twisted cotton of the same size. With the increased strength and the nonelastic nature of a metallic wire, we find much less chance of mesh distortion, and absolutely none where the backings in the later type presses, and the grids in the plate and frame type presses, are properly constructed. This element of press construction should be carefully studied by all manufacturers of filter presses, as it is a highly important feature for efficient filtration, no matter what cloth is used on a given press.

In regard to the best construction of metallic filter cloths, we must take into consideration fineness, strength, and cost, remembering that the finer the cloth, the greater the cost.

A regular square mesh could be woven giving as small an opening as 0.0027 in. with a wire diameter of 0.0023 in., where a square foot would weigh about 1 oz. This would, however, lack the necessary strength, along with other essentials.

By experimental work it was found that a weave could be devised wherein rapid passing of liquids could be obtained without the filter cake interfering with its progress. In its manufacture we have devised a wedge-shaped opening, permitting the filtrate to pass through rapidly, and in turn causing the filter cake to form against a practically solid flat backing. It has been asked why the wedge-shaped opening is used in preference to a round, square, or rectangular opening. A drop of water will not pass through a square or round opening as quickly as through a rectangular opening, for the reason that in the square or round opening it must pass through under pressure, whereas in the rectangular it will naturally elongate and pass through from gravity. With the wedge-shaped opening we have the necessary elongation with the additional element of capillary attraction, because the opening increases from zero to about 0.003 in.

The metallic filter cloth known as No. 250 is equivalent in fineness to the regular 220-mesh, square-weave, wire cloth, with about forty-eight times greater strength. This cloth has been found to be the best for most processes, although it is made in different grades of fineness, for specific uses.

If the precipitate is the product desired, metallic filter cloth can be used without treatment of any kind. In only one industry have we experienced much difficulty in filtration for the saving of the precipitate. That is in the color industry where some of the blues, yellows, and greens are in process. Metallic cloth is not generally satisfactory in this instance, because it will not clog, whereas cotton duck becomes rapidly filled, and clogs in the mesh, holding back the extremely minute particles. Metallic cloth does, however, give very good satisfaction in other color work.

The other phase of filtration involves saving the filtrate. This is of course the most difficult of all in the use of any cloth. It has been found that a finely pulverized fossilized earth, added to the batch or primarily injected into the press, will quickly form a filter cake and permit rapid filtration of the mixture.

For example, a Sweetland press of eleven 8-in. disks was being used to filter liquid soap, to give a clear product. The disks were covered with a heavy grade of cotton duck and, while a fairly clear filtrate was obtained, it was unsatisfactory, and the cotton leaves had to be replaced about every two weeks. Metallic filter cloth was installed in this press, and with the use of fossilized earth an absolutely clear filtrate is now obtained, with the probability that the filter leaves will last for years. Microscopic examinations of a drop of this liquid soap, filtered through the cotton cloths, and evaporated on a glass slide, show star-shaped and very uneven crystals mixed with spots of foreign matter measuring from 0.00016 to 0.0075 in. The samples taken from the metallic cloth and fossilized earth filtrate show a field of star-shaped crystals of the same proportions, mixed with no foreign matter.

The first large industry to use monel metal metallic filter cloth was the sugar industry. Sheets remained in use over two years, whereas the cotton changes had been very frequent. Herewith is a report from the chemist of one of the larger sugar plants:

> In the filter presses handling corrosive liquids in the beet sugar industry, filter cloth made of monel metal is the most successful material that has ever been developed. One of the factors contributing to its success is the possibility of using strong hydrochloric acid to clean it. In the middle of the season the filter cloths are boiled out with strong acid without being removed from the press. As the press bodies are made of cast iron, this allows not only the usual acid corrosion but also a violent electrolytic action.

At the end of the season the filter cloths are removed from the presses and boiled with strong acid, and also scrubbed with metallic brushes. There is no case on record where the cloths have been injured by this treatment.

While many advocate the rolling of metallic filter cloths in order to get fineness, the manufacturers of wire cloth strongly advise against this method, for the reason that the mesh becomes distorted and weakened at the point of contact of the cross wires.

Metallic filter cloth is being used more each year as a liner for centrifugal filters.

Industrial Filter Media

By Arthur Wright

Filtration Engineers, Inc., 253 Broadway, New York, N. Y.

Industrial filtration involves the separation of a comparatively large amount of solids from a small volume of liquid. The rate of flow of liquid through the filter medium is low; hence woven fabrics through which only a small flow is obtainable are used most successfully. Fabrics of high resistance to flow of water through them have for years constituted the typical filter cloth for industrial filtration. To-day cotton duck represents one limit, the dense, and unbleached muslin the other limit, open.

Filter fabrics can be divided into two main classes: those used for neutral or noncorrosive liquors, and those for corrosive liquors. The latter are mainly special media of wool, metal, asbestos, stone, etc. For noncorrosive liquors cotton is the material used almost without exception.

Cotton Filter Cloths

WEAVES—Cotton filter cloth fabrics are made up in duck or plain, twill, and chain weaves. Plain weave has the square or right-angle appearance of all ducking and is woven by the filling or weft passing over one warp and under the next, known as "over one under one." Twill has the diagonal lines so characteristic of its weave, and is made by weaving "over two and under two," with the next filling splitting the warp members. Chain, or as it is also known, broken twill, has a herringbone appearance and is woven with one filling going over two and under two, the next reversing this order, the third being a true twill sequence, and the next repeating the above cycle again. For each weave there is considerable modification, depending on the weights of yarn used and the number per inch. Muslins and drills are trade names for very light duck and twill weaves.

The nomenclature of the various weaves should be better standardized. At present a duck is known by a number (as 00) or by the weight per unit measure (10 oz.). Twill and chain weaves are designated by the number of warp and filling members per inch, as for instance No. 2232, where there are 22 warp members per inch and 32 fillings. There is ambiguity here, for the twills woven of different yarns under the same number of members must weigh differently. A combination of weight per unit and designation of the number of warp and filling members would do much to clarify this.

USE OF MUSLIN—The commercial use of unbleached muslin and other comparatively frail filter cloths marks a distinct advance in the subject of filter media, and represents the application of a principle long understood but impractical until the advent of our modern filters.

Filtration through fabrics should be surface filtration wherein all the particles filtered out of the liquor accumulate on the surface of the medium, as distinct from bed filtration wherein some of the solids are caught through the depth of the filter bed, as in sand or charcoal filters. A thin fabric has not sufficient depth to hold solids within it, whereas thick media will often hold back solids that penetrate the surface. Proof of this is furnished when the surface of a heavy twill or duck cloth will often be quite clean, while the cloth is almost impervious on account of particles lodged within the cloth.

When bag filters, gravity or suction filters, and filter presses were the only agencies at hand, strength of the fabric was the primal specification for all cloths. In bag filters, strength is required lest the weight of the liquor inside the bag burst it, and in tank filters unloading by shoveling out the cake requires a cloth of substantial strength. In filter presses the strength required is not so much due to the pressure of filtration as to the squeezing effect at the gasket joint between the abutting plates and frames. Too much emphasis has often been put on this point. The absolute pressure on the cloth between the plates is not excessive save where the cloth is laid in a wrinkled condition and the pressure has to be increased to stop leakage at such places. To correct carelessness in laying the cloths, strong fabrics were required. For a time, manufacturers of this type of filter were too much engrossed in their schemes of drainage, washing methods, accuracy of machined surfaces, etc., and overlooked the cutting edge of the gasket surfaces. Only a strong cloth would not be cut through by these sharp edges. A rounded edge overcomes this and eliminates the breakage at this point.

FACTORS IN SELECTION OF CLOTH—It is obvious that the yarn used in the cloth is the determining factor in structural strength. It is also important that the cloth be dense enough to make a tight gasket joint when the press is made up. These factors have determined for the most part the specifications of the filter cloth used in filter presses.

Other factors, especially in our modern filters, affect the selection of the best filter medium. The filter cloth is fixed to the drainage member either as a sewn bag, or a wired sheet, or a clamped covering. This precludes quick changes. In consequence a cloth must have an economical life or the attendant expense of replacing the medium will make the entire filter operation excessively costly. Also, in modern filters the discharge of the cake should be without hand labor. This means automatic or semi-automatic discharging methods, the efficiency of which is largely dependent upon the filter cloth used.

Properties Affecting Discharge of Cake

The discharge of the cake from the filter cloth can generally be accepted as a simple matter so long as the deposited cake is entirely on the surface of the cloth. Even with the most freely filtering liquors containing granular solids in suspension, some fine solids penetrate the surface and enmesh in the interior of the cloth. Automatic means of discharge are practically worthless in cleaning the cloth from these solids. Such a condition is fatal to modern type filters, and in some industries where it is almost impossible to prevent solids penetrating the surface of the cloth, as, for instance, raw cane-sugar manufacture, plate and frame filters are still supreme. In these filters the cloth can be changed after each operation. Naturally if the cloth is open or so thin as to prevent the fine particles from collecting within the fabric, discharge of the cake from the surface cleans the cloth.

SMOOTHNESS OF SURFACE—Experience has proved, especially in the case of sluicing discharge, that the surface of the cloth must be smooth for the best results. A duck weave has proved a better cloth than a twill weave of admittedly better porosity.

POROSITY—A new filter cloth held up against the light may show open pores, and yet become positively dense when wetted or in operation for a few runs. In this case the reverse current cannot permeate well and tends to belly out the cloth without lifting the cake away from the cloth. Some operators have had but little better success in discharging when trying out open cloths. A too porous cloth lets the reverse current through too readily, so that it discharges small patches of cake and lets the incoming air pass out through these openings without penetrating the rest of the surface. There is a definite porosity for any particular material being handled, and this can be determined definitely only by actual test.

NAP—The nap or hairy surface of the yarn is of almost equal importance. The nap in the yarn exercises an effect similar to that of the hair in wall plaster. The nap is the loose ends of the cotton and is, of course, greatest in the short staple stock. Egyptian cotton and domestic long staple make cloths of immensely better discharging quality. The costs of these are probably sufficiently high to warrant the proper singeing of the nap from cloths made of short staple. Singeing is generally only surface action, but it is held that with thin fabrics the singeing flame can be regulated to work through the entire fabric. Mercerization of cotton cloths will also reduce the nap but it is not comparable, as a manufacturing process, to the simpler and more easily controlled singeing.

A cloth of only slightly heavier weave than unbleached muslin is used in Sweetland filters for clarifying cane sugar refinery liquors. It has a smooth surface and a high capacity for the flow of liquid through it, and its thinness precludes the possibility of solids lodging within it: hence automatic discharge from it is easily made. There is no gainsaying that it will not stand hard usage. However, any cloth capable of 8 wks.' life under 24 hrs. per day operation must be admitted to be a practical medium.

Selection of Drainage Members

There are means of protecting a cloth so as to increase its life, but none is more effective than adequate support in the drainage member. A screen of 5 mesh per inch or greater should have a protector for light cloths. This can be a lighter or finer mesh screen, or it is cheaper and easier to envelop the drainage member in an open weave burlap. The latter cushions the filter medium against the drainage member and in addition to increasing the life of the cloth it will often be found to add somewhat to its capacity.

Every filter cloth is affected by the kind of drainage under it. Efforts to give the maximum drainage have resulted in excessive drainage in some cases. The foreign presses used in the breweries for sweetening off the mash are examples. The drainage member here is made up of 0.125 in. by 1 in. steel flats spaced at 0.75 in. centers and set edgewise to the cloth. Only a heavy woven fabric can safely bridge these spaces even under a low head of 5 lbs. per sq. in. This drainage member, requiring a heavy filter medium, unnecessarily complicates the operation of these filters. Albuminoidal material lodges in the cloths so that they must be removed after each run, whereas a thin weave could be cleaned *in situ*. If we take the flow from the outlet of a filter element even when the filtrate is flowing fast and distribute it across the entire area of the element, it is evident that the flow through a square inch is hardly faster than in drops at a time. So long as the space for the flow to the outlet does not set up an appreciable back pressure, it is sufficient. In an experiment made some years ago on a free-filtering calcium sulfate slurry, two leaves were connected to a common header and tested under the same suction pressure, with all operating factors maintained constant. One leaf had a drainage member made of wooden slats, the other, using the same-sized collecting frame, had one layer only of a thin burlap. The burlap leaf lagged at first, but in less than 0.5 hr. the cake on both leaves was the same. A large chemical plant recently discarded iron screen drainage members and substituted five layers of burlap and obtained a higher rate of flow. Naturally with a soft drainage of this nature thin cloths can be substituted for the old heavy cloths with marked success.

Requirements of a Filter Cloth

We no longer give primal consideration to the rate of filtration for any cloths. With few exceptions the resistance of the depositing cake to the flow of filtrate is many times that of even dense cotton ducking, so that the initial resistance of the filter cloth is trivial in comparison. This is not true of paper pulp filtration, where only a small suction is employed and where the pulp is free-filtering. The filtering rate of the cloth will be found to be of moment only when its resistance increases with recurring operation due to poor cleaning of the previous loading.

Formerly the first consideration of a filter cloth was its clarifying properties. To-day this is quite secondary. Most operators are realizing that the true filter medium is a layer or film of the solids which are being filtered out of the liquor. Of course, with this in mind, provision must be made for the cloudy filtrate obtained at the start of filtration. If extremely open weaves are eliminated, the amount of cloudy filtrate is not excessive for refiltration, and clear filtrate should be obtained shortly after starting up. When it is indispensable that only clear liquid be obtained, as in the case of cane sugar sirups in refineries, pre-coating the cloths with an inert, free-filtering solid automatically provides the filtering layer.

A novel and uncommon observance of a principle commonly known to all of us came to notice recently. Animal and vegetable fibers used in the manufacture of the ordinary filter fabric are absorbent. In a plate and frame installation handling a mildly caustic liquor the plant superintendent noticed that his cloth failed more quickly in the gasket portion than in the filtering area. The wash water penetrated through the filtering area but failed to wash out the soluble between the abutting gasket surfaces. He made this part of the cloth nonabsorbent by painting it with a tar base paint, thus materially increasing the life of the filter cloth with no noticeable expense.

Allowance for Shrinkage or Stretch

The consideration of shrinkage and stretch of filter cloths is of vital importance. Every cotton yarn shrinks when wetted, and the amount varies, depending upon the physical constants of weaving, that is, the tension under which the cloth is woven, the density of the threads, and the number of intersections. Duck and chain cloths shrink much more than twill weaves. Stretch is the reverse of shrinkage and is due to mechanical pressure, usually that of reversed compressed air in discharging. Twill weaves give much more than any others and make trouble in pressure leaf filters especially. These points must be taken care of by the local user by providing extra material for liquors in which the cloth shrinks and by making up the leaves as tightly as possible where stretching is to be encountered.

Media for Corrosive Materials

So far we have considered the material being filtered noncorrosive to the medium. Alkalies and acids are, of course, hard on vegetable and animal fiber. Some salts like aluminium sulfate have a contracting action, and unstable salts, such as some of the ammonium salts, give trouble. The degree of the deleterious effect depends upon the concentration of the liquor and the temperature. Actual test is the best means of determining whether a cotton, wool, metal, or stone medium is required.

For weak caustics like milk of lime, cotton can be used economically. But wherever cottons are used with even the weakest alkalies, precautions should always be taken that the caustic does not concentrate. Letting a filter stand several days so that the cloth becomes dry before the filter is again put into operation is manifestly poor practice, as the drying of the cloth concentrates such caustic as is present. Wool is the poorest material to use on caustics of any strength. This should be remembered where a cake filtered from an acid liquor, in which wool is a very good medium, is washed with a caustic.

Strictly speaking, the world's best acid filter medium is silica, or other inert compounds as carborundum, alundum, etc. Filtros, a porous fused silica, is typical of this class of material. Mechanically these media do not lend themselves as well to the types of industrial filters most widely used. They are sometimes faulty on account of their lack of uniform porosity and the possibility of solids penetrating the surface, never to be removed.

METALLIC CLOTHS

One of the factors of safety provided in this weave is that any imperfection due to faulty workmanship can be reduced by rolling the cloth between heavy cylinders, thus closing up the imperfection. Much criticism has been leveled at this rolling, on account of the injury to the wires. If the metal is soft enough the rolling has only a small, if any, deleterious effect. If heavier wires of improperly annealed material are used it is quite evident that rolling is a poor expedient.

The improvements in twill weave instead of square weave, strength proportioned to the warp members, monel metal for iron, etc., are later-day improvements making the cloth a better medium. The wire cloth company who turned out the first commercial cloth later perfected a weave from the old Dutch cloth of commerce which has proved to offer some striking advantages. Much heavier wire can be used and the smooth finish of its surface as well as the evenness of its weave are some of its commending features.

In some liquors the metal is slowly attacked so that its life is definite. For such work there can be no discussion as to the kind of metallic cloth to use. The wire of maximum cross-section is desired and the cloth using it should consequently be selected.

CLEANING OF FILTER CLOTHS

The filter medium often becomes fouled as a result of incrustation, either from handling supersaturated solutions or from precipitation caused by lowering the pressure of the liquor. In order that the porosity shall be maintained sufficiently to obtain production, the cloth must be cleaned with an agent that will dissolve the incrustation. This is particularly true of metallic filter cloth used on caustic liquor containing calcium compounds as precipitates. The use of an acid, such as hydrochloric, to remove these incrustations is, of course, fraught with danger to the cloth. In most instances the incrustation is unnecessary. Calcium carbonate will often deposit because the liquor contains bicarbonate. If the temperature had been raised and held at the boiling point the bicarbonate would have broken down to normal carbonate. This is very evident in beet sugar manufacture. There is a safety provision for even these liquors as they are generally handled. In closed outlet filters all that is required is that there shall be a back pressure on the medium above the actual point of precipitation. In practice this back pressure can take the form of a pipe delivering the filtrate to an outlet some feet above the filter. In a magnesia plant the scale that formed on the vertical pipe required a change of a section of the pipe each week. This, however, was a great improvement on having the filter cloth plugged up with this deposit. Of course, this remedy is not applicable to suction filters. In this case pretreatment is the only outlet, and where this is not feasible a different type of machine is probably the solution for successful handling of this material.

Fundamental Laws of Filtration with Suggestions Regarding Research Work

By D. R. Sperry
119 McKee St., Batavia, Ill

[The material covered by the first part of this paper will be found in *Chemical and Metallurgical Engineering*, **15** (1916), 198.]

The fundamental law of filtration developed in this article is:

$$\frac{dQ}{dT} = \frac{P}{\frac{R\%Q}{K} + R_m} \qquad (1)$$

The discharge formula under constant rate of flow conditions may be derived from (1) as follows:

$$\text{If} \quad \frac{dQ}{dT} = \text{constant} = M$$

$$P = \frac{R\%QM}{K} + R_m M$$

$$\text{or if} \quad \frac{2K}{R\%} = W$$

$$P = \frac{2QM}{W} + R_m M \text{ and } Q = \frac{PW}{2M} - \frac{WR_m}{2}$$

where Q = flow of liquid; P = pressure; T = time; K = rate of deposition; R = resistance; % = per cent of solids; R_m = resistance of filter base.

Using the terms W for $\frac{2K}{R\%}$ and N for $\frac{KR_m}{R\%}$, the equation for discharge under constant pressure conditions, developed in the original article, may be expressed as

$$Q = \sqrt{WPT + N^2} - N.$$

SUGGESTIONS AS TO RESEARCH

It should be borne in mind that these expressions are for rigid solids. There should be an investigation as to the effect of pressure upon nonrigid solids. It will of course change both K and R, and to a certain extent R_m.

A table should be made showing the value of K for different substances, and a careful record made of size and shape of the suspended particles, etc.

A table should be made showing the value of R for different substances with full data regarding particles, etc.

An investigation should be made of filter cloths. The value of R_m should be found for various weaves and weights of cloth. Measurements should be made of the strength of various cloths, their coefficient of shrinkage, their ability to stand acids and alkalies, their ability to wear under ordinary treatment, leakage at beginning of runs, etc.

The effect of viscosity upon the fundamental laws should be studied, along with the effect of change in temperature.

The effect of sedimentation should be studied in so far as it influences filtration.

The effect of various filter-base supports should be studied.

The effect of consolidation of adjacent cake formations should be studied, and the effect upon the time-discharge curves.

The effect caused by the addition of different alloys to various mixtures should be investigated.

A study should be made of filter paper and a table made similar to that made for cloths.

Filter bases not made of cloth or paper should be studied.

The effect of feeding filters with different kinds and sizes of pumps should be investigated.

The Feeding of Filters

By J. F. Springer
618 West 136th St., New York, N. Y.

Feeding may be defined as consisting of the transmission under pressure of the unfiltered liquor from a point where it is received from storage to the inlet aperture of the filter.

The necessary equipment will accordingly consist: (1) of the transmission pipe line; (2) the pump or other forcing device which directly or indirectly brings about the movement through the transmission line and effects the pressure of the unfiltered liquor against the filtering medium; and (3) the power apparatus through which or by which the drive of the forcing device is effected.

Treatment of the Raw Liquor

CHILLING—Filtration has for its object the physical separation of solids from the liquid proper. It is highly desirable, however, other things being equal, that the raw liquor be kept in the form of a simple solution while passing through complicated parts of the feeding equipment. Certain classes of filters are competent to deal with certain solutions. Such filters effect precipitation in the immediate vicinity of the filtering media, so that the raw liquor, which enters the filter as a solution, consists at the moment of filtration of a liquid in which solids are suspended. This transformation may be effected, for example, in the standard filter press by providing for the circulation of a chilling brine back of and between the working surfaces of the plates. The incoming solution is chilled as it approaches the filtering medium, and soluble matter contained in it undergoes precipitation.

ADDITION OF PRECIPITANT—It seems to the writer that another method might be used in the press for securing similar results. A great many substances are precipitated from solutions by the addition of certain precipitating substances, which may be solutions, simple liquids, or solids. It might be possible to introduce such a substance into the filter press at points between leaves or elsewhere. The conversion of the solution into a liquid containing suspended solids would occur shortly before arrival at the filtering medium.

The importance of maintaining the condition of solution up to actual entrance into the filter centers largely on the relief this gives to pump and transmission line. One of the greatest problems encountered in feeding is the maintenance of valves and other complicated parts free from deposits of solid matter. It is not absolutely necessary that the transformation from a solution to a liquid containing suspended solids be effected inside the filter. In many cases the transformation point may probably just as well be located at any convenient point on the transmission line between the filter and the nearest valve or other part subject to clogging. This may call for some changes in the character, dimensions, and placing of that part of the transmission pipe between the transformation point and the filter.

REMOVAL OF PRECIPITATE—To carry this point further, there are probably a few, possibly many, raw liquors, in which certain unwanted solids are already in suspension, which may be reduced to simple solutions for passing through that part of the transmission line where clogging is possible. This may often be effected in one of two ways or in a combination of the two: The suspended solids may consist entirely or wholly of material that may be made to settle, it may be possible to dissolve the solids, or both results may be brought about. When such measures are possible the passage through the pump and valve section of the transmission line is wonderfully facilitated. Actual practice today would, upon adequate search, probably show many instances where the foregoing program is partly carried out, more especially the removal from the raw liquor of sedimentary matter which can be settled quickly. Whether the second method of treatment is used, the writer is unable to state.

The means of facilitating deposition of sediment will usually involve the provision of convenient settling basins. Another method makes use of the centrifugal idea. The liquor containing sediment is made to swing round sharp curves or is passed in and out of a machine which causes it to revolve. If the particles in suspension are really of greater specific gravity than the liquid and if the retardation effected by the liquor is not too great, the particles will seek points away from the center of rotation. The same general method has been used in actual practice in freeing air of dust.

Noncorrosive Construction

Some of the raw liquors that must be transmitted in present-day practice will not, however, be made harmless by the measures just described. Some of them are highly corrosive. The obvious answer to this difficulty is to construct all parts in pump or transmission line coming into contact with the corrosive liquor from noncorrosive material, or at least line them therewith.

Lead is a favorite metal for linings and for pipe lines. It interacts very slowly with most substances, as, for example, ordinary sulfuric acid. However, there are limitations to its use. For instance, rain water reacts with lead to form the soluble hydroxide, $Pb(OH)_2$. Nitric acid attacks lead. Concentrated sulfuric acid (sp. gr. higher than 1.700) attacks lead even in the cold. With hydrochloric acid, lead reacts slowly. It is obviously ill-adapted to the construction of moving mechanical parts, because of the lack of the necessary hardness and tensile strength.

Wood resists acids splendidly, but is also unsuited for many moving parts. Recently, hard rubber has come into consideration. It is highly resistant to many corrosive activities, and possesses considerable degrees of hardness, and tensile and compressive strengths. It is also resistant to alkalies.

Cast iron enjoys a good reputation as a material resistant to acids and alkalies. It successfully resists the boiling acid solution of magnesium bisulfite employed in the manufacture of wood pulp. It has been used successfully as the material for the shell of a monte-jus through which is passed a mixture of 40 per cent nitric acid and fuming sulfuric acid. A monte-jus made of wrought iron is said to have been completely destroyed in 24 hrs. Upon examination of the interior of the cast-iron monte-jus after what appears to have been a fair period, no trace of corrosion is said to have been found.

A special iron-like material which is well adapted for use in filters appears to be a kind of silicon-iron. Manganese, phosphorus, and sulfur are also present, though probably only in minute quantities. The material seems to be essentially a gray cast iron with a high silicon content. This material has been subjected to prolonged cold and heat tests by the Bureau of Standards. The cold tests were carried out at a temperature of 15° to 20° C. for about one-third of a year, and the depth of corrosion for the whole year calculated. A few of the results are fairly representative. Sulfuric acid of 95 per cent strength had only the most minute effect, calculated as a corroded depth of 0.0000206 in. in 1 yr. The diluted acid showed greater action, but even the 10 per cent solution effected a depth of corrosion less than 0.0001 in. Nitric acid was still less effective. A 25 per cent solution of hydrochloric acid effected corrosion at the rate of 0.00805 in. per yr. Acetic, phosphoric, oxalic, pyrogallic, oleic, and picric acids were also tested. Other corrosive liquids, such as aluminium potassium sulfate, ammonium chloride, ferric chloride, and copper sulfate, had only insignificant effects, the maximum being less than 0.0001 in. per yr. A 30-day test at 82° to 88° C. naturally produced greater results. With sulfuric acid, the 10 per cent solution effected corrosion at the rate of 0.00156 in. per yr. and the more concentrated solutions at diminished rates. Nitric acid in the higher concentrations effected corrosion at rates well under 0.0005 in. per yr. The 10 per cent solution had more effect. The 25 per cent hydrochloric acid ate into the metal at the rate of 0.366 in. per yr.

Pressure Requirements

All filtration is by pressure, whether the pressure at the filter medium is effected directly by the creation of a positive pressure on the raw liquor on the precipitate side, or whether it is secured indirectly through the removal of the natural air pressure on the filtrate side. In the latter case, 14.7 lbs. per sq. in. would appear to be the maximum attainable under ideal conditions. In elevated regions even this theoretical maximum would be reduced. However, the vacuum method is doubtless vigorous enough for multitudes of cases. Direct pressure may be effected through the force of gravity, by the drive of pumps, and by the tension of compressed air. Still another method, which is said to have been introduced into small filters and in laboratories, depends upon the creation of a centrifugal pressure on the raw liquor, causing filtrate and precipitate both to press against the filtering medium. As the precipitate cannot get through and the filtrate can, the ordinary filtering separation occurs. It is precisely the same phenomenon as occurs under more usual circumstances.

GRAVITY FILTRATION—This requires pumps or an equivalent to put the raw liquor at the proper elevation. Except for the considerable losses through friction, etc., the energy expended in elevating the raw liquor is reëxerted in effecting the filtration. Theoretically, in accordance with theory based on a *few* assumptions as to conditions, each foot of elevation will bring about an increment of pressure per sq. in. amounting to the product of the specific gravity of the liquor by the weight of 12 cu. in. of water. This principle may be stated as:

$$P = 0.434 \times s \times E = 0.434\ Es$$

where P = pressure in lbs. per sq. in., E the elevation in ft., and s the specific gravity of the raw liquor. This formula disregards friction, viscosity, leakage, etc. It may serve, however, as the basis for a broader formula containing a factor to be determined by experiment and then to be used tentatively as a single independent variable is varied.

Used as it stands for highly concentrated sulfuric acid, for example, it means that a 50-ft. head would produce a pressure of 40 lbs. per sq. in. That is, if we assume the highly concentrated solution of 168° Twaddell, the formula gives:

$$P = 0.434 \times 50 \times 1.840 = 39.9 \text{ lbs. per sq. in.}$$

While this formula does not take into account all the conditions that obtain, it is nevertheless useful at the present moment in showing us that considerable elevations will be required, even with heavy liquors, if one is seeking high pressures. The effect of the factors not included in the derivation of the formula would generally tend to the increase of E required to produce a given pressure. To get the maximum pressure required in filtration operations, usually around 150 lbs., involving such a liquor as sulfuric acid, the tank would have to be set at a height sufficient to enable the level of the contained liquor to be maintained at about 187.5 ft. above the filter. It should be remembered in this connection, that high elevations, while they do incur the construction and maintenance of towers, do not reduce the power requirements, since all pressure that gravity exerts in the filtration operation must be expended in putting the raw liquor at the necessary elevation. However, gravity feeding provides for a steadiness of flow and a steadiness of pressure that are valuable. By a sufficient increase in the plan section of the tank, the pressure fluctuation may be reduced almost to zero. For example, if we assume a tank to be 6 ft. in diameter and to contain as heavy a liquor as concentrated sulfuric acid, a variation between delivery of liquor to the tank and withdrawal for feed would have to amount to 2.36 cu. ft. to bring about a 1-in. change in level. This 1-in. change in level, moreover, would cause merely a pressure change of a trifle over 1 oz. (1.06 oz.) per sq. in. It will be seen, then, that with generous horizontal sections, a wonderful steadiness of pressure may be produced. Of course, there will be no pulsation from the pumps or other means of delivery to the tank. Naturally, the pipe line from tank to press must be sufficiently generous in size and so moderate in the number and sharpness of its bends as to insure a good flow of liquor.

Furthermore, an advantage to be credited to gravity feeding is that, for moderate pressures involving moderate elevations, it will often be possible to locate the filter in the basement and the gravity tank in the attic or on the roof, thus obviating the construction of a special tower.

PUMPS—The types of pumps usually employed in connection with feeding are:

1—Steam pumps
2—Power-driven reciprocating pumps
3—Power-driven rotary pumps (including centrifugal)

Any of these may be direct-connected to the filter press or open filter or gravity tank.

In the case of the steam pump it is necessary to consider whether heat is permissible in the particular case. One of the principal builders of filter presses favors the steam pump for all-round service. The speed is under a nice control, and the equipment is inexpensive to purchase and requires but little space for its installation. It is said to be "fool-proof," in that the ratio between pump and pistons may be so selected that the pump will stall at a predetermined pressure. This is a point of especial value, where the steam pump is directly connected with the press and its pressure is directly transmitted to the plates.

Where a power-driven pump is employed it will generally be possible to introduce on the transmission line between pump and filter a special safety valve with pressure indicator and weighted control lever. This valve may in a simple manner be set at a predetermined pressure and thus provide relief inside the press, particularly at the working surfaces of the plates. Ordinarily, the power-driven pump will be without speed control. This may be corrected, however, by using a variable-speed electric motor. These are more or less expensive, and it would seem that, so far as protection against the hazard of breaking plates in the press is concerned, the safety valve would cover requirements.

It may be worthy of note that some concerns using pumps for feeding glycerol, grease, oils, and lard have apparently found a duplex pump suitable. Another concern is reported to be using the same design of pump for handling sulfate of manganese. This pump is fitted with ball valves. When glycerol, grease, or oils are in question, bronze and brass may be used in various parts liable to suffer otherwise.

A power-driven rotary pump is often an inexpensive form of feeding unit, but it lacks ease of control. Sometimes, a valve is placed between pump and press, the object in view being the cracking of the valve when a predetermined pressure has accidently or otherwise been built up. Objection has been made to this form of control on the ground that the valve is liable to clogging from deposited solids.

COMPRESSED AIR—The monte-jus is the equivalent of a pump in which operation is secured through the pressure developed against the liquor by compressed air. There are two general types, one being hand-controlled and accordingly requiring personal attention, the other being automatic. In a representative monte-jus there is a case or tank having several openings above. For instance, immediately in line with the vertical axis may be a central opening through which compressed air is admitted. To one side may be another opening, through which the liquor is admitted to the tank. On the opposite side may be the discharge opening, through which the compressed air at the proper moment forces the liquor. This opening may have passed down through it a prolongation of the discharge pipe. We will now assume that no compressed air is entering the tank and accordingly that the air valve is closed. Upon opening the inlet valve controlling admission of liquor through the feed opening, liquor is admitted. If this valve be closed when a proper charge has entered the tank and the air valve opened, conditions will be right for a discharge of the liquid contents. The discharge valve is opened, and this passage of liquid takes place. In the automatic monte-jus, the opening and closing of valves takes place without attention.

Monte-jus may be made of special chemical stoneware or of metal. In the latter case, they may be specially lined with lead, or the metal itself may be selected so as to provide suitable resistance to corrosion. A monte-jus is especially adapted for use with acids and liquors containing acids. It may be a small affair or it may be of considerable size.

Monte-jus often fit into special conditions. In one instance a filter press had to be fed with a thick granular and acid mixture. No pump could be found for the job. Gravity feed was unsuitable because of the probability that the connecting pipe line would suffer clogging. A monte-jus with a lead lining gave good service. Monte-jus are not cheap, either at the beginning or during operation. The first cost is considerable, and compressed air must be applied to secure action. They are not largely used in the United States but have found considerable application abroad. One great objection to the apparatus is its intermittent action. Under the special conditions where a gravity feed to the filter is permissible, however, the monte-jus may be used to supply the elevated tank without anything but inconsiderable fluctuations in the pressure in the press, provided the plan section of the tank is given a generous area. A monte-jus that is to be used under considerable air pressure may often with advantage be imbedded in concrete.

Filter Aids

By C. P. Derleth

Celite Products Co., Monadnock Bldg., Chicago, Ill.

A filter aid is defined as a substance which may be admixed with liquids to be filtered without affecting the physical or chemical characteristics of the filtrate and which facilitates the removal of suspended matter in the filtering process. Some of the materials which have been used for this purpose are: Asbestos fiber, wood pulp, paper pulp, Filter-Cel, diatomaceous earth and infusorial earth (both known as kieselguhr), magnesia, talc, lime, calcium sulfate, powdered silica, sawdust, and, partly for this purpose as well as for their decolorizing properties, vegetable carbon, animal carbons, and fuller's earth.

The material trade-named "Filter-Cel" is a cellular siliceous product which is especially prepared for filtration purposes, and of exceptional purity. Kieselguhr, which includes both diatomaceous earth and infusorial earth, is a broad term covering material from various deposits found throughout the world. The impurities occurring in these earths affect the filtering efficiency and contaminate the liquid with which they are admixed. Strata of clay are found in most deposits and, since they consist largely of alumina, have the effect of giving gelatinous precipitates, especially in alkaline solutions, which decrease the rate of filtration. Many of these clays are in such a colloidal state that the filtering efficiency of the material is completely counteracted.

Filtration problems may be divided into three classes:

1—Those in which the suspended solids are rigid, and either crystalline or amorphous.

2—Those in which the suspended solids are nonrigid bodies, *i. e.*, those approaching the colloidal state, although they may be far greater in size than those properly classed as such.

3—Suspensions containing mixtures of the above classes.

Filtration of Rigid Particles

Problems of the first class are the easiest to handle. It is necessary merely to choose a proper filtering medium, either cloth or screen. Usually the medium has a sufficiently fine mesh to retain all of the suspended solids from the beginning of the filtration period, but at times it is advantageous to use a medium with larger openings. In this case the suspended solids are depended on to build up, and the cloth or screen becomes, more properly speaking, the retaining medium. The filtration proper starts only when a properly arranged layer of larger sized particles has been retained, preventing the finer particles from passing through and giving true filtration.

In many problems in filtration the suspended solids have been produced by precipitation and crystallization. It is an advantage to secure the largest possible crystals, in such cases, so as to secure a cake having larger pores, thus offering less resistance to the flow of liquid.

In a case of this kind, provided the cake is not to be used, or if it can be subsequently separated from the filter aid, a precoating of the cloths with material of very fine porosity will give initial clarity. According to Hatschek,[1] if the mean distance from pore to pore of the filtering medium is larger than the diameter of the particles being filtered, the first layer will be drawn by the vortices into the orifices of the pores and the medium throttled. It can be seen that if an initial film of very porous material be deposited on the medium the orifices will not be throttled. The network of pores prevents the meshes from being closed up, and each succeeding layer of deposit will form a network so that the whole thickness of the layer or film will be permeable. In addition it should always be kept in mind that it is advisable to work with reduced pressure at the beginning and gradually to increase the pressure as the thickness of the deposit increases. By this means the first layers of the deposit are spongy and porous, and offer little friction to the passage through of liquid, and the high final pressure tends to dry the cake. This precaution will also increase the length of life of the cloths by preventing the sharp corners of the crystals from cutting the fibers of the filter cloths, as a result of the pump pressure applied. Where corrosive liquid is being filtered the precoating of the cloths will give cleavage, allowing the cake to drop off readily, and will prevent the finer crystals from being forced into the pores of the retaining cloth or screen. Where fine mesh screens or metallic cloth are used, a precoating with a filter aid is often desirable to give initial clarity to the filtrate. The precoating may be done by charging the filtering surface with a suspension of the filter aid in water or clarified liquid, returning the filtrate by by-passing for a second filtration. It is easily possible with a good filter aid to retain finely divided crystals, such as barium sulfate.

Filtration of Nonrigid Particles

In a few instances precipitates of the second class can be converted into a crystalloidal state either by proper regulation of the precipitation or by subsequent treatment. This should be done wherever possible, thus converting the problem into one of the first class.

Those nonrigid suspended solids which do not lend themselves to crystallization and which have many of the properties and characteristics of colloids (although they may be much larger in size) constitute the most difficult problems in filtration.

A problem is often rendered more complex by the viscosity of the liquid, as in the case of concentrated sirups or raw linseed oil. In the past, gravity filtration has been depended upon in coping with this type of problem. The downward movement of the liquid toward the filtering medium is so slow that the nonrigid solids settle down until they rest on the surface of the medium without being swept into its pores. As long as they are undisturbed they retain the shapes of the floc. For this reason a centrifugal pump is better adapted for pressure filtration than a reciprocal type, the pulsation of which causes a disturbance of the floc. Even an attempt to speed up the process by increasing the head results in driving the solids through and into the pores of the medium, yielding a cloudy filtrate. If the pores of the medium are fine enough to retain the solids, the filter is plugged and the operation is at an end.

---

[1] *J. Soc. Chem. Ind.* **27** (1908), 539.

Often the nonrigid solids are coagulated by heating or other means, or, if the solids do not lend themselves to coagulation, reagents have been added for the purpose of producing a flocculent precipitate and entangling the fine matter in suspension. The coagulant then collects on the surface of the filtering medium and a small head allows the liquid to trickle through slowly. The disadvantage of this method is the slowness of the operation, necessitating a very large filtering area.

USE OF FILTER AID—If the somewhat uniformly sized particles of a filter aid are added to the liquid containing the nonrigid particles, the gelatinous particles are separated upon being deposited on the filtering medium, layer after layer being built. The porous particles give rigidity to the cake, permitting pressure to be used and preventing the particles from being swept through the pores of the retaining medium, thus making it possible to secure perfect clarity. The pores in the filter aid should be microscopic, the filtration being accomplished more through capillaries than between interspaces of the particles, inasmuch as the interspaces are filled with the albuminous, pectinous, colloidal, or other solid matter.

The volume of filter aid necessary will depend upon the quantity of suspended matter present, the temperature at which filtration is carried on, and the pressure used, as well as upon the viscosity and specific gravity of liquid being filtered, etc., and this quantity can best be determined experimentally, by using an excess of the filter aid, and gradually decreasing the amount added until the rate of flow of the filtrate is retarded, indicating that the surface pores are becoming clogged.

Necessary Characteristics of a Filter Aid

POROSITY—Porosity is a criterion of filtering efficiency. Crystalline bodies such as magnesia and calcium sulfate occupy definite spaces which do not completely cover the surface of the filter, but pack adjacent to each other's edges and surfaces, and have small or large channels according to their shape and size, which being rigid are not affected by pressure and which offer free passage to the filtrate. Particles of a material such as Filter-Cel pack adjacent to each other or adjacent to the particles of suspended matter in the liquid, but because they are porous they can retain relatively larger quantities of precipitate, at the same time maintaining a continuity of pores through the cake to the retaining medium.

REGULARITY OF SIZE—Particles should be as regular in size as possible. Small particles will pack in the interspaces left by the larger grains, reducing the size of the free passages, and causing the rate per square foot of filtering area to be retarded.

INERT MATERIAL—The product should be practically inert. If there is an appreciable soluble matter which would affect the taste, odor, color, or chemical analysis, or in any other way reduce the purity of the liquid to be filtered it will not be effective. Care should be taken in the selection of a filter aid to suit the liquid handled. Hot caustic liquors dissolve silica readily. Magnesia, used on a small scale in pharmaceutical work, is soluble in every acid liquor.

BULKINESS—A filter aid should be light in weight and bulky. It is purchased by weight and used by bulk, therefore its weight per cubic foot in the dry and loose form is an important item. It is important not only from the cost standpoint, but also in the manipulation of the liquor in the filtration process. The particles should settle out so slowly that excessive settling will not take place while the mixture of the liquor with the filter aid is in the filtering equipment. If the material were to settle out rapidly it would not build up an even, porous cake, but would build up solidly from the bottom, and that portion of the cake space filled or bridged would be ineffective for the filtering operation. When the filter becomes about half full of solid cake the rate is so retarded that it is usually not possible to wait until the entire cake space is filled. In the case of a leaf type filter, the heavy material would settle out in the bottom of the shell and seriously affect the rate.

A filter aid should be added to build up an open, porous cake which will fill, so far as possible, the cake space in the filter. This makes possible thorough washing or blowing of the cake to reduce retention of liquid, permits the filter to be cleaned readily, and allows the filter cloths to retain their porosity for longer lengths of time. There is probably an absorption of colloidal matter by the filter aid, as is shown by the removal to a trace of the albumin of milk by a simple filtration with Filter-Cel.

Advantages of Using a Filter Aid

1—Improved clarity of filtrate.

2—Saving in power due to reduction of pressure.

3—Less loss of liquid by cake retention, because a firm dry cake is built.

4—Increased extraction through ability to wash cake.

5—Less labor in cleaning cloths, also less redressing.

6—Decreased cloth expense.

7—Increased rates resulting in greater capacity of filtering equipment.

8—Makes possible the use of labor-saving types of pressure filters for clarification filtrations.

9—Complete separation of solids from liquids without the use of chemical defecants, and without affecting chemical composition of the filtrate.

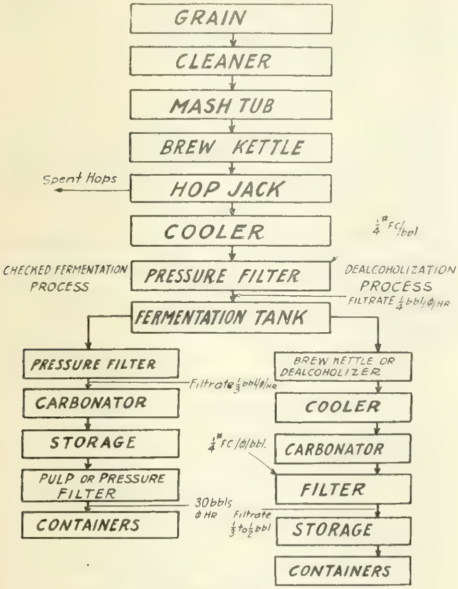
The Use of Filter-Cel for Industrial Filtration Processes

By G. M. Hickey
Celite Products Co., New York, N. Y.

In every filtering operation in which the filtrate is of value, and in cases where the cake is dissolved, Filter-Cel can be used to an advantage. In order to show the wide use of Filter-Cel to filtering operations, its application in four typical industries is outlined: the manufacture of cereal beverages; the refining of coconut oil; the hydrogenation of oil and production of glycerol from soap manufacturing; and the production of cider and allied products from the pressed fruit juice.

Cereal Beverage Filtration

The former method of manufacturing cereal beverages involved long settling processes, after which the beverage was easily clarified with a pulp filter. The present low alcoholic content of cereal beverages presents a different problem and two new methods are used: the checked fermentation and the dealcoholization process. In either one there is a large quantity of suspended solids that must be removed. Some manufacturers mix Filter-Cel with their pulp to give a finer filtering medium and aid in the filtration. Other companies use standard types of pressure filters with Filter-Cel. The beverage is made as outlined on Flow Sheet 1. The first filtering is after the wort leaves the hop jack, to remove the albumins, hop resins, etc. Using 0.5 lb. of Filter-Cel per bbl. a rate of flow of 1/3 bbl. or 10 gals./sq. ft./hour is obtained.



Flow Sheet 1—Cereal Beverage Industry

The filtrate then goes to the fermentation tanks, where it is fermented to the desired alcohol content. Filter-Cel is again mixed with the wort, 0.25 lb. per bbl., to filter out all the yeast cells and slimes, producing a sterile beverage that can be stored in a moderately cool cellar without danger of further fermentation.

In the dealcoholization process the beverage is filtered from the hop jack, cooled, and permitted to ferment to a high alcoholic content. It is then settled and run back to the brew kettle or dealcoholizer, where the alcohol is driven off. The beverage is cooled and filtered with Filter-Cel, using about 0.5 lb. per bbl. to remove the yeast cells, albumins, and other particles left in suspension after boiling. In many cases the beverages are filtered after carbonation and in order to prevent foaming a back pressure of about 10 lbs. is placed on the filter. The filtrate is either allowed to go back to storage or can be bottled directly from the filter. In these operations Filter-Cel not only produces a sterile, crystal-clear beverage, but prevents the cloths from sliming and simplifies the cleansing of the cloths.

The comparative costs of filtering 200 bbls. of cereal beverage in a pulp filter and a pressure filter with Filter-Cel, not including the initial cost of pulp, are as follows:

Pulp lost in operating and washing	5.00
Water for washing pulp	3.20
Steam for washing pulp	6.10
Labor for washing pulp	7.50
	21.80
Water for cleaning pressure filter	.16
Labor for cleaning pressure filter	1.50
Filter-Cel for filtration—200 bbls.	3.00
	4.66

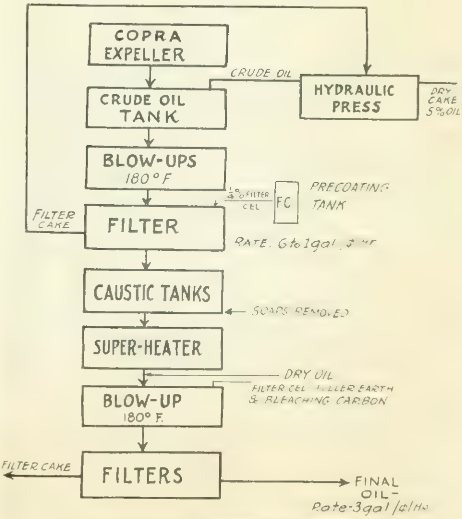
This shows a saving of $17.14 per 200 bbls., or $0.085 per bbl.

The use of a pressure filter with Filter-Cel in these operations entirely eliminates the use of paper pulp, and saves the time generally taken in the washing and regeneration of pulp and molding the pulp cake for the filter, making a big reduction in labor necessary to operate the filtering station. The use of Filter-Cel permits the immediate clarification of the beverage at any stage, without settling.

Coconut- and Vegetable-Oil Refining

In the coconut-oil industry economic filtration has always been a problem, as the nature of the oil varied so that it was very hard to find any method of filtration that would cover every condition. The general means of handling crude oil from the expeller is with a pressure filter, using a heavy filter paper over the cloths to insure brilliancy of the filtrate. This also prevents the slimes from embedding themselves in the cloths. If this oil contains a large percentage of slimes, they make an impenetrable coating on the paper so that no further oil can pass through, and the press requires immediate cleaning. This is expensive, both in time and the amount of oil absorbed in the filter paper, as it is usually thrown away after each operation. By precoating the cloths with a heavy coconut-oil suspension of Filter-Cel, using 10 to 15 lbs. per 100 sq. ft. of filtering area, the use of filter paper is eliminated; this suspension is then followed through with the main batch of oil containing approximately 0.25 per cent of Filter-Cel in suspension. The amount of Filter-Cel used will vary, however, with the nature of the oil. The Filter-Cel and the slimes and foots deposit themselves on the cloths, building up a porous cake that can be readily dried and easily discharged. It is not necessary, however, to spend considerable time drying out the cake, for in refinery practice it is returned to the hydraulic press where it is finally pressed, reducing the oil content to about 5 per cent. In addition to the saving of material and time by using Filter-Cel in this operation, the type of oil produced is of a higher grade. This clarified oil gives a minimum amount of trouble with emulsions during the caustic treatment.

The crude oil from this process passes on to the refinery where it is treated with caustic to neutralize the free fatty

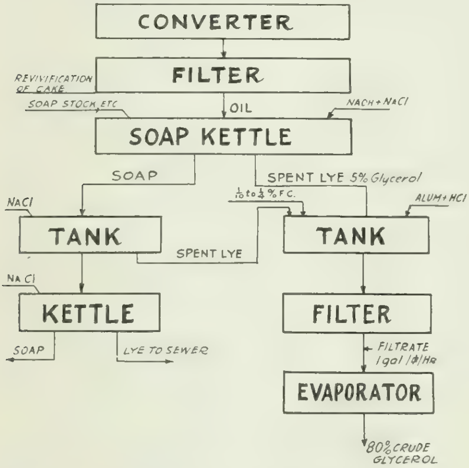


Flow Sheet 2—Coconut Oil Industry

acids. The soaps are skimmed or drawn off, and the oil goes to the superheaters where it is dried. The oil is given a final treatment and polished with a mixture of Filter-Cel, fuller's earth, and bleaching carbon. The addition of Filter-Cel to this mixture aids in the filtration of the oil and builds up a porous cake. The amount of Filter-Cel used is generally 0.1 to 0.25 per cent. When the filtering operation is complete, the press is blown out with either superheated steam or air, to reduce the oil in the cake. By using this mixture, in plant operations, the percentage of oil in such a cake has been reduced from 18 to 8 per cent.

Oils, Soap Lyes, Etc.

In the hydrogenation of oil a most important feature of the process is the recovery of the catalyst. It is very difficult to retain this finely powdered metal in a filter press. Since the finished oil must be absolutely free of the metal, Filter-Cel is added, clarifying the oil and retaining the metal completely.



Flow Sheet 3—Hydrogenation of Oils and Spent Lye Recovery in Soap Plants

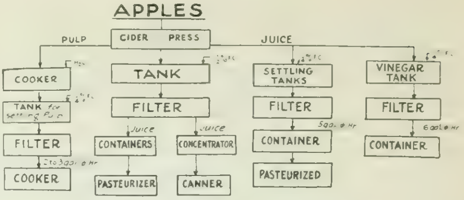
When nickel salts are used, Filter-Cel, because of its light weight, is used as vehicle to keep the catalyst in suspension. The fact that Filter-Cel is insoluble in acids makes the recovery and revivification of the catalyst most simple.

In soap plants the hydrogenated oil is pumped into the soap kettles, with other soap stock, and given a caustic treatment. This throws out the soaps leaving crude soap lye which contains about 5 per cent crude glycerol. This is pumped to a tank where the lye is neutralized with acid and alum, and about 0.1 per cent of Filter-Cel is added. The mixture is filtered to remove the slimes, delivering a clear glycerol sweet water. The rate of filtration is about 10 to 12 gal. per sq. ft. per hr.

The Filter-Cel eliminates the slimes usually encountered at this point, increasing the capacity of the filter station. The cake discharge is so perfect that the cloths do not require washing, and can be used over immediately. The filtrate is water-white and after evaporation is a high-grade crude glycerol. The removal of suspended matter prevents foaming in the evaporators.

Filtration of Fruit Juices as Typified in the Apple Products Industry

The use of Filter-Cel in the treatment of apple products brings out the tremendous advantage of clarifying a food product mechanically without affecting the delicacy of flavor, food value, etc. The fresh apples are taken to the press or the mill, where the juice is extracted and either disposed of as cider, concentrated apple sirup, or cider vinegar. The pulp is sent to the cookers where water is added to extract various ingredients and this is filtered and the filtrate concentrated into pectin or apple jelly.



Flow Sheet 4—Apple Products Industry

With the combined use of a pressure filter and Filter-Cel, freshly crushed cider is filtered, using a precoating of 15 lbs. of Filter-Cel per 100 sq. ft. of filtering surface and 0.25 per cent Filter-Cel in the pressure liquor. This produces a brilliant cider with a rate of flow of about 4 gal. per sq. ft. per hr. With sufficient care in bottling and pasteurization a sterile beverage can be placed on the market that will not become cloudy or turbid with age. The filtered juice may be concentrated to 30° Bé., making cider sirup. This product retains its rich amber color. If unfiltered cider is concentrated it has a dirty brown color.

Cider vineger is clarified with 0.25 to 1 per cent of Filter-Cel, with a rate of flow of about 6 gal. per sq. ft. per hr. This produces a brilliant product that remains clear. The settling out of the slimes in the vinegar is eliminated by removing the yeast cells in the filter. Owing to the acidity of fruit juices, vinegar, etc., wooden plate and frame presses are most suitable for these filtrations.

The pulp from the mill is placed in a cooker, where water is added, and boiled. The liquor is drawn off and filtered with 0.3 per cent of Filter-Cel, giving a rate of flow of about 2 to 3 gal. per sq. ft. per hr. The clear filtrate is then concentrated into pectin. As a result of the finely divided and slimy nature of the suspended solids, this separation was formerly carried out by settling or with crude gravity pulp filters which was very ineffective and impractical.

Centrifugal Filters

By H. C. Beckman

The DeLaval Separator Co., 29 East Madison St., Chicago, Ill.

The precipitation of sediment from a liquid by subjecting the mixture to the action of centrifugal force is finding application in a number of industries. In many instances such centrifugals have supplanted filters and are frequently spoken of as centrifugal filters, but there is nothing about such apparatus to justify the use of the word "filter," since the liquid is not passed through filter material. Such centrifugals properly belong to the class termed "clarifiers."

It is to be understood, therefore, that this paper limits itself to centrifugals in which the liquid to be treated is forced through filter material, although it may be stated in passing that clarification plays a more or less important part in nearly every type of centrifugal filter.

Centrifugal filters may be divided into two general classes:

1—Those in which the drum is perforated.
2—Those having an imperforate drum.

Perforated Drum

The former class has found but limited application in the commercial world outside of the sugar industry and the drying of crystals, etc. There is some doubt of the propriety of characterizing centrifugals used in these instances as filters, for while the cake which forms in the periphery of the drum is probably more or less of a filtering medium, the function of the machine is more essentially that of a centrifugal extractor of the type used in laundries, for drying clothes. However, similarly constructed machines have been used rather extensively in an experimental way.

The serious drawback to this class of filters is the fact that the action of the centrifugal force constantly tends more firmly to pack the residue that has accumulated on the filter base, quickly rendering the mass impervious. We have here a vicious circle. The greater the force, the more densely the residue becomes packed against the periphery, and the more densely it is packed, the greater is the amount of centrifugal force necessary to force the liquid through. Furthermore, a filter of this class has no particular advantage over a standard type of plate press, and differs from it only in that the pressure is derived from centrifugal force instead of from gravity or a pump, both of which have a pronounced advantage over centrifugal force from the standpoint of expense and convenience.

Imperforate Drum

Centrifugal filters of the second class lend themselves to the application of an important novel principle. The force developed may be utilized not only to supply the pressure required to force the liquid through the filter, but, of far greater importance still, also to prevent the accumulation of residue on the paper. The surface of the filter medium remains clean and the filter is in substantially the same condition at the conclusion of a run as at the beginning.

On first thought it would seem that this novel principle might best be utilized by employing the filter medium as a tube in the center of the bowl, the passage of the liquid being from the outside towards the center and the residue being deposited on the outer side of the filter, from whence it would be most easily dislodged by the centrifugal force. Experiments, however, have given negative results. It is impracticable to dress this type of filter properly with filter paper, and the centrifugal force tends to open up the paper. In the most approved construction, the filter base is held horizontally, or in the same plane in which the drum revolves. The liquid to be treated is forced by the hydrostatic pressure due to centrifugal force to pass up (or down) through the filter paper, leaving the sediment on its surface. The flow of liquid through the paper is at right angles to the direction of the centrifugal force, and as soon as an appreciable amount of residue has accumulated the centrifugal force dislodges it and deposits it in the periphery of the drum.

ADVANTAGES—Liquids carrying a slimy sediment, or one made up of particles that tend to "shingle over" or seal the paper, may be filtered as easily as ordinary liquids. Since the filter does not lose its efficiency, the filter area may be very small; many gallons may be filtered through a few square inches of surface. In the filtration of expensive liquids, such as pharmaceutical preparations, physiological serums, high-priced varnishes and lacquers, etc., this factor presents an important advantage, since the loss due to absorption by the filter medium is materially reduced. Incidentally, this type of filter permits the utilization of the principle of centrifugal clarification, for the liquid is automatically subjected to clarification *before* it reaches the filter paper. The gross impurities are thrown out by centrifugal force; the filter paper has only to remove the lighter flock or cloud.

DISADVANTAGES—The limit as to size is low. The largest drum that has been found commercially practicable thus far is about 10 in. in diameter by about 8 in. high, fitted with twenty filter plates 7 in. in diameter. This drum is operated at 6000 r. p. m. It has a dirt or sediment-holding capacity of between 110 and 125 cu. in. Such a machine will filter from 10 to 200 gal. per hr., depending upon the density of the filter paper and the viscosity of the liquid.

High-speed centrifugals call for a high degree of mechanical excellence. An unusual degree of care is necessary in their manufacture, which makes the price relatively high. While the operator need not necessarily be a skilled mechanic, he should have a higher degree of intelligence than a plate press operator. That centrifugals of this type are thoroughly practicable from a mechanical standpoint is demonstrated by the fact that thousands are in operation in plants where the care they receive is far below what would be given them in the ordinary type of industrial institutions.

DISCUSSION OF CENTRIFUGAL DRAINING

By T. A. Bryson

Tolhurst Machine Works, Troy, N. Y.

Filtration in centrifugal machines is accomplished by the application of centrifugal force to remove liquids from solids. The action may be compared with that of a gravity filter in which the separation of solids and liquids is brought about by the force of gravity. Aside from the modifications in apparatus used, the difference in the two methods is largely in the amount of separating force employed. In the gravity filter or drain table the force is of a fixed magnitude; in the centrifugal filter the separating force may be made, within practical limits, of any desired amount.

In analyzing the force producing draining, let us consider a stone whirled rapidly upon a string. The centrifugal force so generated will be evidenced by tension in the string.

If W is the weight in pounds of the stone, R the length in feet of the string, and N the number of revolutions per minute, the centrifugal force (C_F) will be

$$C_F = \frac{W\ R\ N^2}{2932}.$$

If there were no whirling and the stone were merely suspended by the string, the tension due to gravity would be W.

The ratio of the tension caused by centrifugal force to that caused by gravity is therefore

$$\frac{C_F}{W} = C_R = \frac{R\ N^2}{2932}$$

in which we may call C_R the centrifugal ratio.

By referring to the centrifugal ratio we do not have to be concerned about the weight of any particular body of solid or liquid. Whatever its weight, W, may be, the centrifugal force acting upon it will be WC_R; or the force acting upon a unit volume of liquid will be $w\ s\ C_R$; where w equals the unit weight of water and s the specific gravity of the liquid.

Applying this to the centrifugal basket in which the solids are retained, we have at any point in the load at a distance R′ from the axis of rotation, the centrifugal ratio:

$$C_R = \frac{R'N^2}{2932}$$

It follows that the draining force varies directly as the distance from the axis and as the square of the revolutions. For any given speed the force is entirely dependent upon the distance from the center and the variation of the draining effort lies within the limits of the inner and outer surface of the load as determined by the width of the basket ring.

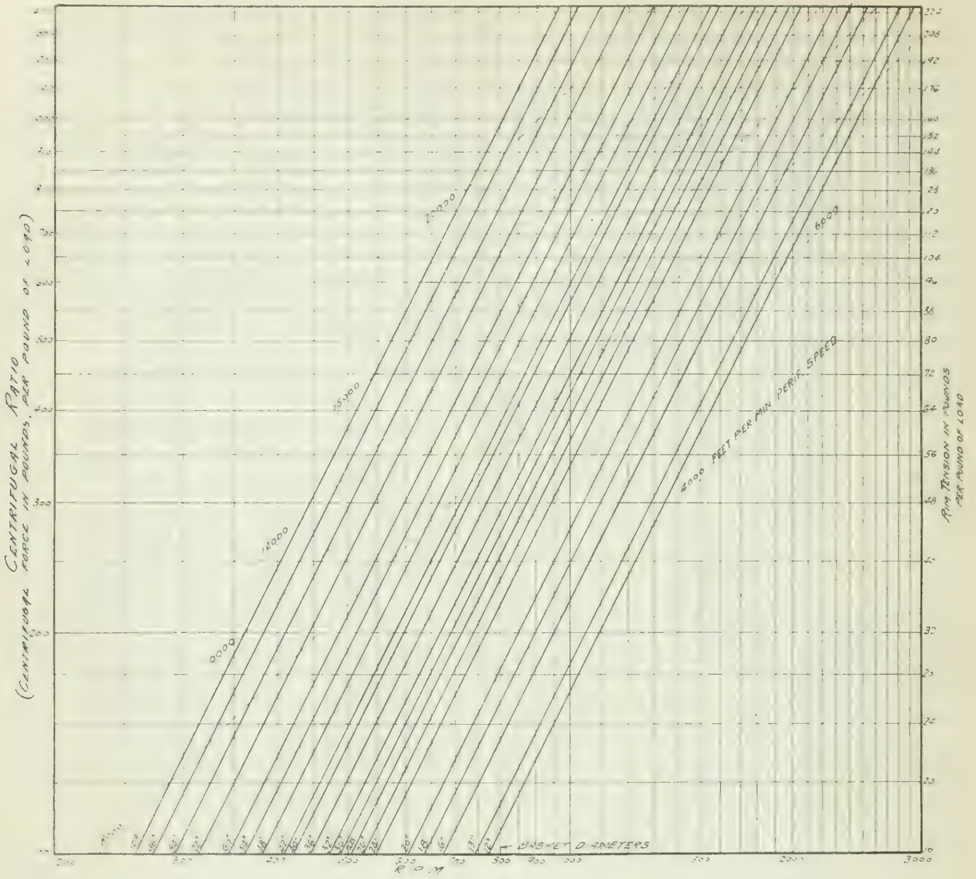


FIG. 1

Usual practice is to make R_1, the inner radius of the basket ring, about 0.7 R_2. If R_1 is made less than this, the interior surface of the load has too great a reduction of draining effect, the load is more difficult to reach in discharging the basket, and with finely divided materials there is more danger of clogging due to the thickness of the wall. We therefore measure the effectiveness of the machine by reference to the relation of the centrifugal force to that of gravity.

The above chart shows this relation with various basket diameters and speeds. The values given are for the periphery of the basket, and the average force acting on the charge would be somewhat less, probably in the neighborhood of 85 per cent of the values given.

FACTORS AFFECTING DRAINAGE

The dryness which may be obtained in a centrifugal depends upon several factors.

Assuming a coarse granular or crystalline material without a great excess of liquid, the moisture in the mass to be treated is in contact with particles of solid. The liquid clings to particles with a tenacity dependent upon the surface tension and the area of contact. It is drawn from the particle with a force equal to the weight of the liquid multiplied by the centrifugal ratio. The weight of the liquid depends obviously upon its specific gravity and its volume, which latter is governed by the interstices between the particles of solids. The maximum dryness is obtained when sufficient liquid has been removed to leave a film of liquid so thin that the centrifugal force developed by its weight is too small to break down the surface tension. Until this condition of equilibrium exists, there will be an unbalanced force tending to move the liquid toward the periphery. The time required for the liquid to find its way out depends upon its viscosity and the size of the openings in the mass of solids, through which it must pass

We may then sum up the factors affecting the draining as follows:

REMOVING FORCE:
  1—Centrifugal ratio
  2—Specific gravity of liquid
  3—Volume of liquid

RESTRAINING FORCE:
  4—Surface tension
  5—Area of contact of liquid and solid

RESISTANCE TO MOTION:
  6—Viscosity
  7—Size of openings in the mass

Factors 3, 5, and 7 are all governed by the size of the solid particles. The more finely divided particles will present a greater surface area for a given volume of liquid and the smaller channels for the passage of the liquid will further restrict its flow.

It is therefore to be expected that the more finely divided materials will require a longer time to drain and more moisture will be retained when equilibrium is reached.

It is obvious that the physical characteristics of any wet material may vary between wide limits and from hour to hour during production. For this reason it does not seem that any great hope is offered in presenting the factors governing draining in mathematical form.

Even the effect of centrifugal force may not be expressed as a continuous function, for experiments have shown that with many materials there is a maximum centrifugal force above which it is not advisable to go. This is especially noticeable with finely divided materials which may often be handled more satisfactorily at comparatively low speeds, particularly during the earlier stages of dewatering.

If a charge of finely divided material is quickly subjected to high centrifugal force there is a tendency for the cake to be spun up on the basket side sheet in an almost impervious wall. The outer layers—those nearest to the basket sheet—seem to be so densely compacted that the passage of the liquid from the interior is prevented or greatly retarded.

When there is a sufficiently large percentage of liquid in the charge, free liquid will collect on the inner surface of the cake.

The conditions are now more similar to those obtaining in a filter press. The wet material is quite fluid and the machine is invariably charged while running. As the cake builds up in thickness, the resistance increases due both to the longer distance the liquid must travel and to the increased squeezing action at the periphery occasioned by the hydrostatic head within.

If the speed of the machine is maintained low, not only during charging, but for some time thereafter, until the major portion of the liquid is removed, the total time required for the operation will probably be shortened.

When the solid particles are slimy or soft, it is possible that the high centrifugal force actually deforms them and the free area between the particles is closed up. With very fine solids, which are not soft, it is possible that there may be a question of the arrangement of the particles under the influence of centrifugal force.

It is claimed that particles collecting on a gravity filter under the comparatively low force of gravity, arrange themselves in cubical piling. This gives the maximum volume of voids between the particles and therefore the greatest cross-sectional area for the passage of liquid. It is probably true that under reasonably low centrifugal force the same condition obtains. When the centrifugal force is very high at the time of charging, it is conceivable that the particles might be driven into hexagonal piling which is the most stable arrangement, but it would make the exit area for the liquid a minimum.

It has been shown in practice with these fine materials that if the majority of liquid is removed at a low speed and the cake sufficiently dewatered to reduce its fluidity, the basket may then be brought to full speed, causing a noticeable increase in volume of effluent and much less tendency for the cake to become impervious. This would seem to indicate that the deleterious effect of high centrifugal force at the beginning of the operation is due more to the arrangement of the particles than to the closing of the openings by actual deformation.

By maintaining the particles in cubical piling until the fluidity of the cake is reduced to the point where they are less liable to rearrangement, a larger draining area is maintained.

In any case it is advisable to use the lowest speed that will give satisfactory results. This means less strain on the machine and, where corrosion of the basket may have weakened it, greater safety. In this connection: never speed a machine beyond the manufacturer's rating. The centrifugal force and consequently the strain upon the basket increases as the square of the speed. Frequent inspection of the basket is advisable, especially if corrosive materials are handled.

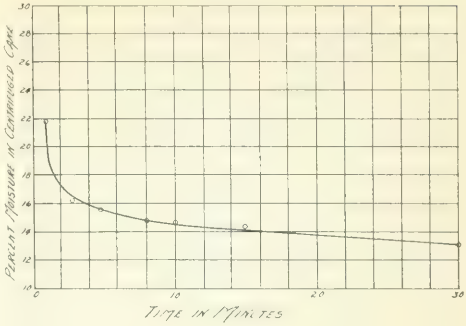


Fig. 2

Fig. 2 illustrates a typical draining curve which in this case is plotted from tests on sodium fluosilicate. After the machine had been run for a given time a sample of the cake was taken by pushing a thin-walled tube through the cake and withdrawing a plug of solids. This method avoided errors in sampling if there were any difference in dryness between the inner and outer surfaces of the wall. The per cent moisture is computed on the basis of extracted material (moisture plus dry solid equals 100).

Fig. 3 shows a washing curve in which the volume of wash water is plotted against specific gravity of effluent.

Compensation for Unbalanced Loading

The most important factor from the design standpoint is that of unbalanced loading of the basket.

Good practice demands that in charging the basket, the material be as evenly distributed as possible. Much effort has been made to construct machines which will automatically adjust themselves to unbalanced loads, with the result that the compensating devices employed have become the distinguishing features of the several types of machines.

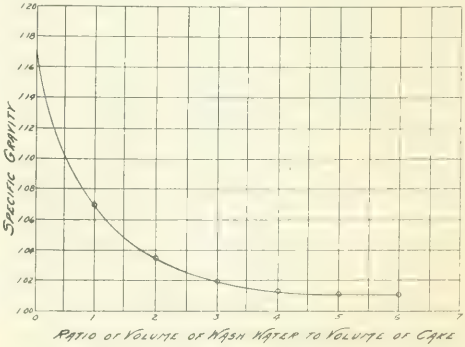


Fig. 3

Suppose a basket were loaded so that 20 lbs. more weight were placed on one side than the other and that the machine were speeded to develop 500 lbs. centrifugal force per lb. of load. The force produced by the excess weight would be 20 × 500 = 10,000 lbs. This force would tend to pull the basket and spindle away from the center and would act in a constantly changing direction like the pull of a stone whirled on a string. To resist such a force would require excessively heavy construction, and would cause severe vibration in the machine, in addition to the great waste of power in bearing friction.

If, however, the spindle were allowed perfect freedom, the rotation would take place about the center of gravity of the loaded basket. In other words, the basket would automatically revolve about the point in respect to which the load were balanced. This would cause a gyrating or whipping motion of the spindle.

This self-balancing characteristic of rotating bodies is taken advantage of by the builders. In practice, perfect freedom cannot be allowed, as it is necessary to provide restraint sufficient to prevent excessive gyration and to counteract certain disturbing forces which are common to high speed rotors.

Practically all centrifugals are equipped with bearings which allow gyration to a greater or less degree. In one type the bearing box is mounted in a rubber cushion or is controlled by steel springs. Another method is to mount the bearing boxes rigidly in the case, which is itself allowed to sway under the influence of the unbalanced load, the inertia of the case being sufficient to permit only a slight oscillation. A third type depends upon the action of gravity to control the motion of a sliding step bearing.

Maintenance

Centrifugals should be substantially supported; preferably on a concrete foundation. The feet or base of the machine should have a good even bearing and the anchor bolts should be kept tight to prevent rocking. Poor installations are the most frequent causes of unsteady running. When machines are set on wooden upper floors, it is well to place them over or near a girder and to tie together the beams underneath so that the load will be distributed; in this way preventing the floor from yielding in spots and causing vibration.

As in all high-speed machinery, lubrication is of prime importance. For machines designed for oil lubrication, a fairly heavy engine oil has been found to give the best results. For the thrust bearing, particularly in the large machines where the load supported is heavy, a thin oil will be forced from between the bearing surfaces. As a general rule, the heaviest engine oil which will not gum and clog the oil channels or ducts should be used. Oiling should be done regularly. A thorough inspection and refilling of oil cups at the beginning of each day or each shift is an excellent practice.

Where there is a question of the use of centrifugals, probably the only satisfactory procedure is to let the centrifugal builder make tests of the material to be handled, from which he can predict fairly closely what may be expected under operating conditions.

[In this discussion, Mr. Bryson showed a large number of slides illustrating compensating and discharging equipment, and the application of the centrifugal filter in various industries.]

Pulp or Filter Mass Filters

By E. E. Finch

The Karl Kiefer Machine Co., Cincinnati, Ohio

Pulp filters, as they are commonly called, are filters in which a mass of cellulose is formed in filtering layers as the filtering medium. They are used for filtration purposes to to clarify the product, but we should not confuse the fact that clarification and filtration are not always the same.

One of the first filters of this type introduced into this country consisted of a series of plates, vertically arranged, and in these plates was compressed a form of mass or pulp as the filtering medium. Measured from the standard of today, the filter of course was very crude and unsatisfactory. Rubber gaskets were used, a procedure which would not be tolerated at this time.

A little later on another type of German filter was imported, which consisted simply of a large brass or copper cylinder in the center of which was a perforated pipe. The mass was packed loosely into the cylinder around the pipe, the product entered at the side, filtered through the mass and escaped through the perforated center cylinder.

The development of the large pulp filters began about 1900. Manufacturers were working along different lines, under different patents, and various types were built. It was soon proved, however, that the type that must be used was one that would permit of high pressure, but that would at the same time prevent the possibility of imperfect filtration. It was seen that the filter itself should be made of either copper and tin or of special bronze, and that the filtering material must be of the highest quality and most carefully selected and prepared. It was found necessary that great care be used in the construction of the filter itself. Only the highest grade of pure copper could come in contact with the product and in most of these filters the copper was coated with a heavy coating of pure block tin.

Another very important point, and one that exists at this date, is the question of the filter mass or filtering medium. The success of any filter very largely depends upon the preparation and care of the filter mass. Too much emphasis cannot be placed upon this one point.

In the handling of the great variety of products, such as fruit juices, tonics, elixirs, perfumes, and also various food commodities, in which the odor or flavor may be seriously affected, the selection of the filtering material is of prime importance. Various fibrous products have been used, such as wood fiber, linen fiber, cotton fiber, asbestos, and infusorial earths. Wood fiber should never be used, because it is coarse and flat and lacks resiliency. Linen fiber is not to be considered. Asbestos, if properly treated, may be used sparingly at times and has some advantages. Infusorial earths may be used occasionally for certain commodities, but there is always the danger of such materials affecting the flavor and aroma of the product handled.

The best filtering medium is a pure cotton mass. It has great resiliency, and by the use of either short or long fiber, a filtering layer may be produced to suit the operating conditions. It may be used repeatedly without any ill effects, provided it is properly washed so that the fibers are not balled or knotted.

Preparation of Filter Mass

The filter mass is first dissolved into a soft mass, without balls or knots, and then formed into what is commonly termed a filter cell. In small filters this is usually a single cell. In large filters a layer consists of a double cell. This cell usually is a layer of mass from one-fourth to two inches in thickness.

The layer or double cell is usually formed in a hydraulic press, before placing in the filter, and thus can be carefully examined by the operator. The pressure used on the hydraulic press varies from 20 to 50 lbs., according to the product that is to be handled. These layers are superimposed, one above the other, in the filter. Between the layers is placed a coarse-mesh screen which acts as the inlet conductor. In the interior of the layer of mass are two fine-mesh screens with rib centers which act as outlet conductors for the filtered product. If the layers are not properly formed and in the process of filtration considerable sediment collects on the filter plates, the pressure of the pump increases, and there is the possibility of this pressure breaking through the layer of pulp and into the outlet, allowing the unfiltered liquid to pass through.

To overcome this, the mass around the center outlet is compressed to three times that of the rest of the layer, or, in other words, is compressed to bone hardness. The coarse-mesh screens, before referred to as being placed between the layers, have heavy bronze centers that fit into these depressions and thus, if one layer is placed above the other, it makes a compact, elastic filtering column. Each layer is a filter in itself. The product does not pass through first one layer and then the other. On account of these compression centers, it is impossible for the cloudy liquid to break through, even though the pressure may reach 100 lbs. This type of filter will block with sediment and it is impossible for any unfiltered liquid to pass through into the outlet.

Sizes and Types of Filters

The filters are made in various sizes and types to suit the requirements of the user. It is very essential that the user secure from some source information as to the type and size of filter he should use. Often we find that the manufacturer hesitates to accept the advice or the help of the filter manufacturer, with the result that he is never adequately equipped. Certain chemicals must not come in contact with bronze. Alcoholic preparations must not be handled on iron filters. Products containing a great deal of acid should be handled through filters that have been heavily silver plated. If the purchaser will frankly put his problem up to the manufacturer of filters, he will receive unbiased and valuable information.

Pulp filters to-day are a necessity for many manufacturers who desire to clear liquid products. The use of these filters is not always understood and perhaps a few illustrations may be of interest. At this time there is a great demand for filters for the clarifying of fruit juices. Manufacturers frequently desire to filter this juice immediately as it is pressed from the fruit. This, however, cannot be done. The fresh fruit contains a certain amount of pulp and glutinous matter that will block the filter almost immediately. The manufacturer is usually impatient and feels that some filtering device must overcome the trouble. Frequently a great deal of money is spent in trying to secure such devices when they cannot be supplied. The trouble can be overcome by one of three methods:

1—By pasteurizing or cooking the juice immediately, filtering, and then effecting a second pasteurization when the product is in the bottle. This method is not desirable, however, with many products, for the reason that the heat causes them to lose their fine flavor and aroma.

2—A very advantageous method is to chill the product, bring it down to a temperature of about 34° to 35° F, then filter, bottle, and pasteurize.

3—By running the product into tanks, and allowing it to stand from 4 to 12 hrs., depending on the room temperature. While the product is thus at rest, a considerable amount of precipitation occurs. Draw off and filter without disturbing the sediment, and immediately pasteurize in bottles.

Pressure to Be Employed

Another feature of filtration is that with certain products a high pressure can be used, while with other products a very low pressure of only a few pounds should be utilized. Olive oil is a very delicate product and must be handled carefully with but little pressure.

Recently there was brought to the attention of the writer an interesting experiment in the filtration of glue. A chemist of experience, a leader in his particular field of work, had devoted some time to the problem of properly clarifying a certain type of glue. During his research work he had endeavored to secure results by filtration, but had been unsuccessful. He then visited one of the large filter manufacturers and conducted his experiments in their laboratories. He found that at just a certain temperature and pressure, excellent results could be secured.

A few years ago it was found possible to clarify gelatin by means of a pulp filter. Necessarily the filters must be of large area and able to withstand the high pressure. I believe it safe to state that all the gelatin produced in this country to-day is filtered through pulp filters.

Let me leave this one suggestion: I do not wish to appear as holding a brief for any filter manufacturer, but I do commend that the prospective user of a filter present his problems to the filter manufacturer and secure his coöperation.

Leaf and Rotary Suction Filters

By G. D. Dickey

Industrial Filtration Corporation, 115 Broadway, New York, N. Y.

Vacuum filtration was first successfully employed in the latter half of the 19th century in Belgium. An ordinary rotating drum with a perforated surface was covered with a filtering medium and hung in a container. In the interior of the drum, vacuum was created, and it was found that the liquid was readily drawn through the filtering medium, while the solids formed on the surface of the drum an even layer which could be scraped off on the opposite side, leaving the filtering medium relatively free.

This trial was made on bicarbonate of soda, which is, of course, a very free-filtering material, and therefore the presence of a thin layer constantly remaining on the filter drum did not retard the rate of flow. The old drum type of apparatus is still used on this class of work, and for many years no attempt was made to apply it to other substances.

Suction filtration, like all other methods of separating solids from liquids, is dependent upon pressure differences. Offhand, therefore, it would seem as if creating a vacuum should, in effect, be the same as the application of direct pressure. Thus the practical limitation of 30 in. of vacuum would mean that the maximum results obtained by vacuum filtration would be equal to those of a press exerting 15 lbs. pressure. A careful study of the many underlying factors which enter into filtration shows that this does not hold true, principally since the formation of the cake itself plays a large part in the results obtained.

The success of vacuum filtration is due to a large extent to the fact that the cake built up is of uniform density and thickness throughout, thereby causing equal resistance to the flow, both of the mother liquor and of the wash water. This uniform cake formation is caused by the fact that the vacuum is operative behind the filtering medium, is equal at all points, and cannot be increased with increasing resistance. Thus, packing of the first layer of the cake against the filter cloth with increasing thickness of formation is avoided, and as the atmospheric pressure is relatively low, a porous cake is formed. Microscopic examination of a cross-section of filter cake formed by vacuum shows almost perfect uniformity throughout.

There are, of course, many kinds of material which, because of their finely divided state or colloidal nature, will not form any appreciable layer under vacuum. This discussion therefore applies only to those materials which are of a crystalline base, or slurries to which foreign crystalline material has been added as a filtering aid, and which are amendable to vacuum filtration.

Determining Factors in Selecting Vacuum Filtration

The ability to form a cake from 0.25 to 0.5 in. or more in thickness, even though many hours are required, is a determining factor as to whether or not vacuum filtration can be employed, and the time required for this cake formation determines what type of apparatus may be used. Two extreme examples are: that of starch, where a cake of 2-in. thickness can be built up in approximately half a minute, and that of some ore slimes, where 8 to 10 hrs. are required for building a 0.5-in. cake.

There are two other determining factors in cake formation. The first is the percentage of solids to liquids present, and the second is the temperature at which filtration may be carried on. Of course, the greater the proportion of solids to liquids the more quickly is the cake formed. It would seem that the old law which states that "when particles approach each other by a distance less than three times their diameter they have a tendency to clump" holds good in most cases. This is especially noticeable in ferric hydrate, for instance, where vacuum filtration is practically impossible in suspensions as dilute as 1 to 15, but when a concentration of 1 to 1 is obtained, the material filters so freely that the rotary filter can be employed. Temperature is also a very important item in filtration. Generally speaking, materials filter much more freely when hot than when cold, owing to the lowered viscosity of the mother liquor, and its consequent freer passage through the filtering medium. Certain oils, for example, cannot be handled at all when cold, but filter quite freely at a temperature of 90°.

Despite the fact that, theoretically, vacuum cannot be maintained on boiling solutions, there is always enough condensation in the pipe lines to enable 28 in. to be maintained on slurries which are filtered at the boiling point. An example of the increase in the filtering rate is in the handling of calcium carbonate, the filtering rate, and subsequent cake formation of which is increased 150 per cent by raising the slurry from room temperature to that of boiling.

There is another aid to cake formation which enables many slurries to be handled which otherwise could not be, and that is the addition of some foreign material, such as Filter-Cel, in the handling of fruitjuices. Ordinarily, if Filter-Cel in the proportion of 1 to 2 per cent of the weight of the solids is added, a marked increase in the cake deposit, as well as in the rate of flow, is noticed. This is due to the separating of the particles, so that a more porous cake is formed, which builds more quickly and offers less resistance to the flow of the filtration. The addition of from 1 to 1 to 1 to 5 parts of Filter-Cel to solids enables practically any slurry to be handled. When such a large amount is added, the cost is often prohibitive, and therefore a balance between the economy of increased and porous cake formation, and the cost of the foreign material added, must be worked out. In many cases, the foreign material can be subsequently recovered and re-used.

The choice of filtering medium should always be carefully considered. However, if the general policy of getting a medium sufficiently coarse so that the solids form their own bed and filter through themselves is followed, good results can be depended upon. Often, the filtrate will be cloudy at first and it will be necessary to refilter, but this can be done readily unless too large an amount of solids has run through.

Washing in the Suction Filter

An equi-resistant, porous cake is very easily washed and dried. The washing is practically by displacement, the mother liquor held in the cake being pushed ahead of the wash water as a wall. This has been proved in actual practice by plotting a curve of the Baumé value of the filtrate. The filtrate maintains its high degree for a certain length of time after washing is commenced and then drops abruptly to about 2 per cent of its former strength. Sampling of the cake at this point shows a washing of about 98 per cent, and the remaining percentage of mother liquor is apparently held as a film around the particles as they lie one upon the other in normal piling. The last portion of mother liquor is removed more or less by diffusion, but can nevertheless be accomplished with a minimum of wash water, because there is an equal passage of wash water through the cake at all points.

In filters of the open tank type, where any quantity of wash water desired can be drawn through the filter cake, an exact amount can be determined upon, if it is desired to save the washings. On the other hand, when the object is to get a thoroughly cleansed filter cake, washing can be carried on for a long period of time.

With a machine of the rotary filter type, the time of washing is more or less fixed by the revolution of the filter drum, and very exact requirements in washing can be accomplished only by the discharge of the filter cake, pulping, and refiltering. The ordinary limit on the rotary filter, without recourse to pulping, is around 1 per cent. This can be definitely figured out by determining the percentage of mother liquor in the original filtrate, and the percentage of moisture in the filter cake. Mathematically, with the increase in the proportion of solids to liquids due to filtering, there is a corresponding decrease in the percentage of mother liquor present. If to this is added a 50 per cent reduction for washing, and the cake is now re-pulped to a 1 to 1 slurry, there will be a certain proportion of mother liquor in this second slurry. Following the same procedure for the second filtration, the amount of the mother liquor left in the second discharged cake can be closely figured out without making any filtration tests.

Very often, the efficient washing of the filter cake is entirely destroyed by the cracking of the cake before washing commences. There are several ways of obviating this difficulty. In the open tank filter, the basket may be raised and the cake dried until cracking commences, and resubmerged one or more times before the cake building is completed. This method takes up the shrinkage of the filter cake to a large extent, and permits transfer to the wash-water tank before cracking can occur. The cutting down of the vacuum, of course, is a great aid to reducing cracking, but often this cannot be done because the cake would be so wet as to fall off during transfer.

In rotary filters, cutting down of the vacuum may be employed more successfully to eliminate cracking, as there is not so much opportunity for the cake to slough off. Rolling or smoothing down of the filter cake by external attachments is often used to iron out the cracks. Finally, if an unlimited amount of wash water can be used, the cake can be enveloped in the wash water from the point of emergence to the point of discharge, so that there is no chance for cracking to occur.

Drying and Discharging the Filter Cake

The drying of the filter cake is dependent to a large extent upon the formation of the cake itself. A cake which is uniform in porosity and thickness can be more or less readily dried by drawing air through it, and, because of its porous nature, is easily calcined or otherwise reduced to powder form after discharge. Ordinarily, the thinner the filter cake the more easily it is dried, although there is not a great difference between cakes of 0.25 to 0.5 in.

In discharging a cake from the open tank filter, the use of steam, water, or compressed air frees the filtering medium cleanly, and no scraping is required. In the rotary filter, if a thin layer left on the filter drum materially cuts down the rate of flow, air pressure may be applied just prior to the scraping of the cake or just afterwards, as the filter drum enters into the unfiltered slurry. The object of the air pressure, of course, is to clean the filtering medium by reversing the action of cake building.

Types of Suction Filters

The three main types of suction filtering apparatus are: open tank filters, continuous rotary filters, and continuous rotary hopper dewaterers.

open tank filter—This consists of a unit or basket composed of a number of plates or leaves, fastened together and connected to a common header. Each of these leaves is constructed of a pipe frame, usually in the form of a rectangle, over which is drawn the filtering medium, sewn in the shape of a bag. The open or loose ends of the bag are held tightly together at the top by means of wooden clamps. The two sides of the filter cloth are held apart by parallel wooden strips set upright, and the filtering medium is stitched in such a manner as to hold the strips in position. Along the bottom of the pipe frames are perforations, causing the suction to pull uniformly at all points when applied behind the filtering medium.

In operation, the basket is submerged in a tank containing the slurry to be filtered, and suction is applied behind the filtering medium. The clear filtrate is drawn through the filtering medium, pipes, and header to the desired point, while the solids are deposited on the surface of the filtering medium. After a cake approximately 0.5 in. or more in thickness has been built up, the basket is transferred, by means of a hoist and trolley, to a tank of clear water. Suction is kept on during this operation. During washing the effluent can be switched to another tank, thus making possible a separation of filtrate from wash water.

After washing, the basket is shifted to the discharge platform, suction still being kept on, and the filter cake is dried by drawing air through it. Discharge is accomplished by shutting off the suction and applying air, water, or steam pressure through the same line. This discharge not only frees the solids from the filtering medium, but leaves it clean for the next cycle.

One of the disadvantages of the open tank type of filter is that in discharging the filter cake, the compressed air or steam causes a portion of the entrained liquor to be blown back into the cake, and a higher moisture content is obtained than would be the case if scraping could be successfully employed. The second disadvantage is that considerable head room is required for the hoist and trolley which must be used for shifting the filter basket. Finally, a cake of at least 0.5 in. should be built up upon the surface of the filtering medium in order to insure a clean discharge.

The advantages are that any period of time of cake building, washing, and air drying that is desired can be decided upon by the operator. The formation of the cake can be followed very closely by raising the filter basket from time to time. Increased filtering area can be obtained by the simple addition of filter leaves, so that a very large square area can be obtained in a comparatively small space. The fact that the filter can be cleaned automatically and the entire operation carried on without any set limits gives this filter a great advantage over any fixed type. At the same time, it is semi-automatic, requiring but a small amount of labor. The uniform porous cake formation gives maximum working with minimum wash water, and the discharge of a cake of this nature means economy in final drying.

ROTARY FILTER—The rotary filter of the multiple compartment design consists of a drum whose periphery is divided into a number of uniform compartments, each being connected by a separate pipe line to the central valve hub, which is cored out to receive these lines. The compartments are covered with a wire screen suitably supported, and over this, encircling the entire drum, is stretched the filtering medium, each compartment being kept separate and distinct, and giving a smooth peripheral surface to the drum. The valve hub rotates against a stationary valve cap, which is so arranged that each compartment can be subjected to suction as well as pressure during any portion of the cycle. Provision is made in the valve cap for applying suction and for drawing off the filtrate and wash water separately if desired. The filter drum is hung in a hopper bottom container, which is provided with mechanical agitation. The scraper constantly removes the filter cake as the drum revolves. Washing is accomplished by means of sprays on the surface of the drum just after it emerges from the container with its accumulated solids.

In operation, the container is kept filled with the slurry to be filtered, and suction applied to the compartments through the valve. The solids are thus picked up, washed, dried, and carried away during every revolution of the drum, while the filtering medium is automatically cleaned by air pressure, either just before or just after the solids are scraped off.

The limitations of rotary filtration, of course, are that the solids must be relatively free-filtering and must be in sufficient proportion to enable a cake of 0.375 in. or more to be built up during a 4-min. period, because it is usually not economical to revolve the drum slower than one revolution in 10 min. A balance must also be worked out between the thickness of the cake formed and the washing and drying of this cake, in order to determine how fast the drum should turn to get the best results.

The great advantage of the rotary filter is that its operation is continuous and automatic, thereby practically eliminating labor and saving an immense amount of time. Large capacities can be obtained upon a relatively small filtering area because of the continual automatic cleaning, and the cost of operation is remarkably low. The advantages of a uniform porous cake for washing and drying, outlined under the open tank filter, are equally true in this type of filter.

ROTARY HOPPER DEWATERER—There are other types of filters similar to the rotary filter; for instance, the rotary hopper dewaterer which is used for solids which are too heavy to be made to adhere to the surface of the filter drum by suction.

This machine consists of a series of hoppers provided with filter bottoms arranged radially about a central shaft. Each hopper, just below the filter bed, is connected to a valve hub by means of pipe lines which permit suction to be applied to the hopper during any desired arc in the revolution.

In operation as the hoppers rotate they are charged from an overhead chute about 30° before they reach the zenith. At this point suction is applied and continued through an arc of approximately 90°. Here suction is automatically cut off and the hoppers discharged either by gravity or by the aid of air pressure.

The solids may be washed before discharge by means of a sprinkler equipment.

The points of advantage and disadvantage are practically the same as those of the rotary filter, except that the depth of the hoppers can be varied according to the material to be filtered, thereby increasing or decreasing the capacity of a given machine.

CAPACITIES OF DIFFERENT TYPES—In conclusion, there may be cited a few examples of what capacities may be anticipated with the three types of suction apparatus. Of course, as previously stated, the capacity of any apparatus varies with the material to be handled; and even with materials which are of the same nature, there is sufficient variation in plant manufacture to cause a considerable degree of variation in filtration results.

In handling sulfur black in the open tank type of filter, a capacity of 200 lbs. per sq. ft. per day of 24 hrs. is usually averaged; or in clarifying lime water 1500 gal. per sq. ft. per day of 24 hrs. In the case of the rotary filter a capacity of 2000 lbs. of calcium carbonate in caustic soda manufacture or 1000 lbs. of cement from cement slurries can be averaged per day of 24 hrs. With the dewaterer, a capacity of 2 tons per sq. ft. per day of 24 hrs. upon the dewatering of slate ground by the wet process or 1 ton of crystals in copperas manufacture is the usual tonnage obtained.

Plate and Frame Filter Presses

By E. C. Alford

T. Shriver and Co., Hamilton St., Harrison, N. J.

Of the many designs and makes of filtering machines that have been produced, the flush plate and frame, and recessed plate types enjoy the reputation of being the simplest and most efficient machines on the market. Their extreme simplicity of construction and operation is probably the outstanding feature of their superiority. Owing to this simplicity, a filter press is to a large extent independent of the "personal equation" and is as far as possible fool-proof, and cheap unskilled labor can be easily trained to produce satisfactory results.

Description of Press

A filter press consists of two end supports, rigidly holding two horizontal steel bars. Resting on these side bars are a number of recessed plates or flush plates and frames, the plates having a drainage surface with a machined portion around the outer edge forming a joint surface. The cloths are held between the joint surfaces and act as gaskets in preventing the material that is pumped into the press from leaking out.

One end of the filter press frame holds a screw fitted with a closing device for pressing the recessed plates or the plates and frames together. This squeezing presses the cloth tightly between the machined surfaces and is not for the purpose of pressing the liquid from the solid, as is sometimes believed by the uninformed. When the material to be filtered is pumped into the press it enters a series of cloth-lined chambers which are "in parallel," that is, each is fed from a common channel and each discharges separately. In the open delivery press they discharge through individual cocks into an open trough; in the closed delivery type they discharge into a header which is piped through the head of the press and connected to a pipe line. The pressure with which the liquid is forced into the filter forces the liquid through the filtering medium. The filtrate flows along the drainage surface of the plates and out, either through the outlet cocks or into the internal closed outlet channel.

During the initial stages of filtration, the pressure rarely goes above 2 or 3 lbs. per sq. in. The filter cloth gradually ceases to be the actual filtering medium as the deposit of solids on its surface increases. Therefore, the thicker the deposit or filter bed, the greater is the resistance to the passage of the liquid and the closer the particles are driven together. The filtration pressure gradually increases until a maximum pressure is reached at which efficient filtration ceases.

Washing in the Plate Press

In its capacity to wash the cake of residue quickly and thoroughly the plate and frame filter excels. The cakes are formed in closed chambers and are therefore solid and supported on all sides, so that there is no possibility of the cake falling from the cloths, resulting in imperfect washing.

Properly formed filter press cakes must of necessity always be uniform throughout. Should there exist soft centers or a settling out of coarser particles, that portion of the cake would be more porous. The flow of the solution, following the line of least resistance, would be of greater volume at such a point than at any other, and a greater amount of solids would be deposited there, until the cake offered a resistance to the flow equal to that of any other portion of the cake.

With the cakes of even permeability formed by the press, high efficiency washing is obtained by admitting the washing liquid back of the cloths. In this way, the wash covers the whole surface of the cloth before penetrating the cake, and all portions of the cake are washed equally.

It must be remembered that efficiency in washing is largely dependent upon the homogeneity and hardness of the cake, which, in turn, is determined by the maximum pressure used during filtration. Therefore, accurate comparative results in washing can be obtained only when the cakes are of equal thickness and hardness. This fact is often overlooked and leads to erroneous conclusions in regard to the washing efficiency of filter presses as compared with other filtering devices. As no air is necessary to hold the cakes in place, there is no possibility of cracks developing in the residue. Such cracks prevent thorough washing.

After the washing operation, air blown through the cakes in the filter press produces a low moisture content.

Filter presses are built to employ positive pressure in filtration.

Recessed Filter Presses

In recessed filter presses the cake is formed between two recessed plates, the thicker edge of these plates forming the joint surface and the recess, when two plates are brought together, forming a chamber in which the cake is made. Recessed plate filter presses may be of the open or closed delivery type, and may be either washing or nonwashing. A recessed press, however, is not an efficient washing press, because of the fact that a recessed cake always has a more or less soft core around the feed channel, and the edge of the cake is thinner than the body of the cake. This is the result of the gentle slope from the joint surface to the deepest part of the recess, which is necessary so that the cloth may be gradually stretched to conform to the recess. If the construction were otherwise, the cloth would be stretched so violently that it would break under the pressure at the inside of the joint surface.

The thickness of cakes in a recessed press is limited by the fact that the cloth cannot be stretched too much or its life will be very short and the cloth upkeep would be enormous. In most cases the depth of recess is limited to 0.625 in., making a cake 1.25 in. thick. If for any reason a thicker cake is desired, it is necessary to use spacing frames between the plates or to use a flush plate and frame pattern press.

Recessed plate filter presses are generally of the center feed type, although in some cases the feed inlet may be located in the upper center or in one corner of the plate.

Plate and Frame Presses

Flush plate and frame presses may be either washing or nonwashing, and open or closed delivery. The method of feeding plate and frame presses divides them into two general classes: those with internal and those with external feed channels. In the internal feed press, all feed channels are through internal eyes which are cast in the plates and frames inside of the joint surfaces and are connected to each chamber by cored inlet ports in the frames, through which the liquid is admitted. In a washing press, the washing or alternate plates have cored ports connecting the drainage surface of the plates with the washing channel for the admission of wash water back of the cloths. In a closed delivery press, similar ports connecting with the discharge channel are provided in every plate.

The internal feed press requires cloths with holes cut in them to correspond with the holes in the plates. When the cloths are draped over the plates the holes in the cloths should be opposite one another and in direct line with the holes in the plates and frames which form the internal channels.

In the case of the external feed press, which is the type more commonly used, the feed and washing channels are in external lugs cast integrally with the plates and frames. These lugs are made tight by means of rubber collars. On the feed side the collar is inserted in the plate so that it does not interfere with the inlet port in the frame. On the washing side the collar is inserted in the frame so as not to interfere with the washing ports in the plate. These collars are so made that, when the press is closed, the rubber is pressed against the metal, making tight joints around the external channels. The main advantage of a side feed press is that no holes need be cut in the cloths. The cloths are merely cut long enough so that when draped over the plates they will cover both sides and extend a few inches below the bottom edge of the plates to allow for possible shrinkage. Should the cloths shrink there are no holes to get out of alignment. The cloth should be wide enough to extend beyond the finished joint surfaces of the plates, but not so wide that the edges will reach the finished surface around the holes in the lugs which form the channels.

Another advantage of the flush plate and frame press is that, since there is no recess in the plate, filter paper may be used as well as filter cloth. The manner of applying the paper is first to put the cloth over the plate, and then drape a sheet of filter paper over the cloth. The cloth between the paper and the filtering surface supports the paper. Paper was used formerly considerably in filtrations, but the present procedure is to use a filtration aid such as infusorial earth, which not only is cheaper than paper but produces better results.

In a plate and frame press, frames can be made of any practical thickness.

Flush plate and frame presses are the most efficient washing presses. The cake, being of uniform thickness throughout, offers a uniform resistance to the washing solution, and can therefore be washed free from soluble material with a minimum amount of washing liquid.

Construction and Materials

Filter presses are usually made of cast iron. Such presses are suitable for neutral or alkaline liquors. Presses for acid liquors or for filtering such materials as colors, pigments, etc., which would be stained or discolored by contact with iron are generally made of wood. For strong sulfuric acid solutions they may be made of hard lead, or for special purposes they may be made of bronze or other metals.

WOOD—Wooden plates and frames are made of a variety of woods, but, on the whole, resinous woods are considered best, as they have the greatest uniformity of grain and undergo smaller shrinkage and expansion in use. They are also less liable to warp in contact with aqueous solutions. The most commonly used material, and the best for most purposes, is selected yellow pine. The wood used must be free from knots and blemishes of any kind, and the more resinous it is, the better. Wood of small, fine grain is better than wood with a coarse grain. Presses made of this material will stand hydrochloric acid up to 10 per cent and sulfuric acid up to 25 per cent, if used cold. Yellow pine presses will not stand hot solutions, as the hot solution extracts the resin from the wood and makes it weak and spongy. Wooden filter presses are not recommended for hot solutions, but where a hot solution must be filtered in a wood press, maple or oak is the best wood to select. Cypress is very acid-resistant but is rather too soft for filter-press use. Too much care cannot be taken in the construction of wooden filter presses, as a poorly made wooden filter press is an item of constant expense, loss, and annoyance. The plates should be made so thick that they do not warp easily, and all joints should be as smooth and perfectly made as possible.

The making of a wooden filter press requires the highest class of wood working skill. Even though the best procurable lumber is purchased, much of this must be discarded in the final inspection. Wooden presses should be set up as soon as made, and kept moist under pressure; otherwise the plates and frames are apt to warp and leak. After a wooden filter press has been used and is put out of service for a time, it should be thoroughly washed with water to remove all mother liquors so that they will not concentrate by evaporation, and attack the wood. The press should then be kept tightly closed and full of water.

In starting up a new wooden press, the tie rods should be loosened until they are only hand-tight, and as the wood expands, the nuts should be backed off so that they will not cut into the wood. A wooden filter press is not tight when made, but becomes tight with swelling. Wooden plates are generally made with corrugated filtering surfaces.

FILTERING SURFACES—There are various types of filtering surfaces: fine grooves, coarse grooves, various sizes of pyramids, double crimped wire cloth, and perforated plates. The most important point is that the channels should be deep enough and narrow enough so that they will not be closed by the cloth being forced into them by the internal pressure. In the second place, the cloth must be supported on a minimum area so as to cut down the amount of nonfiltering surface. The filtering surfaces should be smooth, with no sharp corners or points to cut the cloths. In order of efficiency, the pyramid surface comes first, followed by the corrugated surface, with the perforated screen last. The pyramid surface generally used is about 25 per cent more efficient than any other types of drainage. It holds the cloth away from the surface of the plate and allows free passage of the filtrate through and back of the cloth. At the same time it supports the cloth on numerous points of small area.

In a grooved surface there is much more supported area which is nonfiltering than in the pyramid surface. In the perforated screen the only active area is the cloth over the holes. The relative areas in the generally made types are: pyramid surface 100, grooved surface 73, and perforated screen 30.

CLOSING GEARS—The closing gear most commonly used is a screw and ratchet. This ratchet is provided with a bar of the proper length, and the smaller-sized presses can be closed by one man. In the larger-sized presses, however, a gear and pinion is furnished with a ratio of 4 or 5 : 1. This facilitates tight closing with less exertion, although it takes longer.

Another method commonly used for large installations is the hydraulic closing device, in which the screw end of the press is fitted with a hydraulic ram which operates against the follower and closes the press. With this equipment, which necessitates a hydraulic pump and accumulator, all that is necessary to close the press is to open a valve. In some cases two pressures are used in closing a press: a low pressure which is drawn from the ordinary city main or plant supply closes the press part way. The low pressure line is then closed and the high pressure line opened, and a pressure of from 800 to 2000 lbs. is put against the ram. This closes the press tightly, and the valve may then be closed, for the water that is behind the ram will keep the press from opening. In some cases, however, a locking device is employed so that the high pressure may be released.

In opening the press, the mechanical hold-in is released and the release valve opened, whereby a set of cast-iron weights pulls back the ram. The press is then discharged as usual by hand.

Modern Leaf Type Filters

By Robert C. Campbell

United Filters Corporation, 65 Broadway, New York, N. Y.

While the principle of leaf type filtration has long been known, it is only in recent years that filters employing it have been developed beyond the stage of a few special machines, each with a very limited range of usefulness. The present high standing of leaf type filters is the result of development of suitable "filter machines" to utilize this principle most efficiently. The outstanding feature recommending the filters to be described is simple and substantial design, capable of modification for a wide range of problems.

The common filter bag, through which the liquid passes by the force of gravity, is generally found unsatisfactory for commercial purposes where large volumes of material must be handled with expedience. Such a filter is, of course, limited to the effective pressure produced by the force of gravity, but its greatest drawback lies in the laborious cleaning operation which involves the taking down of the bags full of mud, turning them inside out, washing them and hanging them up again.

If, however, such a filter bag is sewn over a wire screen frame which will hold the two sides sufficiently far apart to allow a drainage space between them, say a quarter of an inch, and a pipe nipple connection is made as the only outlet from the interior of the bag, this filter leaf, as it is called, may be submerged in an open vessel of sludge and by the application of a vacuum to the nipple, the clear liquid may be drawn through the cloth, up the drainage space and out through the nipple, while the solids in the sludge are retained in a uniform layer on the outer surface of the bag. This is the simplest form of leaf type vacuum filter.

Again, if this leaf is mounted in a closed tank so that the nipple extends out through a stuffing box in the wall as the only outlet therefrom and an inlet to the tank is provided through which sludge can be admitted under pressure, the clear liquor will be forced through the filter cloth. This is the simplest form of leaf type pressure filter.

Description of Kelly and Sweetland Filters

These machines consist of a series of filter leaves mounted parallel to each other and at equal distances from center to center within a tank designed to stand the required pressure and of such construction that the leaves can be completely exposed for cleaning in a moment's time by means of an automatic opening device.

In the Kelly filter this tank is cylindrical in form, set horizontally and provided with one removable head which is clamped in place by means of an automatic locking device. The filter leaves are supported on a carriage attached to this head so that when the head is unlocked and withdrawn the leaves are brought completely out of the tank and in full view for cleaning. In the most modern type the whole opening operation is accomplished automatically by means of an air motor, controlled by one four-way valve.

The Sweetland filter consists of a horizontal, cast-iron, cylindrical tank, split longitudinally into an upper and lower half. The upper half is supported on suitable legs at each end, while the lower half is hinged to and supported from the upper at the rear in clamshell fashion. This half is counterbalanced and is free to swing open and closed between the two legs at the ends of the filter. Inserted rubber gaskets are used in both types to insure a tight joint.

When it is desired to discharge the cake from a Sweetland filter the lower half is swung down back from beneath the leaves, allowing the cake to be discharged directly into a suitable hopper or cart.

In the Kelly filter the leaves are rectangular and as they are attached to the movable head they must have their outlets through it to a suitable receiving trough. The circular Sweetland leaves have individual outlets through the top of the filter provided with individual shut-off cocks and sight glasses leading to a common closed manifold pipe.

The feed and drain connections for the Kelly are brought through the very bottom of the shell. The feed to the Sweetland is brought in at one end of the upper body, thus allowing a rigid pipe connection, thence through a cored passage to a distributing channel along the very bottom of the filter. Drain connections are provided from the lower body but it is also possible to blow the excess sludge or wash water back through the feed line in monte-jus fashion by admitting compressed air at the top of the filter.

Other connections generally used include an air vent from the top of the body to release the entrained air when filling the filter with sludge, steam or air connections to the filter body to facilitate draining it or to dry the cakes, and steam and air connections to the filtrate manifold to inflate the filter bags when discharging the cakes.

Operation

A complete cycle embodying filtration, washing the cakes, air drying, and discharging them is as follows:

The air vent is opened and the feed turned on. As the sludge fills the body the air is forced out through the vent. When all the air has been displaced the vent is closed. The pressure then builds up in the filter, forcing the liquor through the cloth. Filtration proceeds in a manner similar to a plate and frame press, except that the feed is stopped before the cakes on adjoining leaves build together. It is generally planned to leave a space of from 0.5 to 1 in. between adjoining cakes to allow efficient washing, and also to allow room for the bags to be inflated when discharging the cakes. If, in the specific problem, the volume of excess sludge between the cakes is small in comparison with the volume of the cakes, the wash water may be followed through behind the sludge and a very efficient wash obtained. If the volume of excess sludge is relatively large there would be a considerable mixing of excess sludge and wash water in the body of the filter and a higher percentage of water would be required to produce a satisfactory wash. In this latter case it is advisable to drain the excess sludge, using about 5 lbs. of compressed air to hold the cakes in place while draining, and then to fill the shell with water, thus completely submerging the cakes in fresh water which, when forced through them, produces a most efficient wash.

After complete washing of the cakes, the excess water in the filter is drained out, using a low air pressure, the drain valve is closed and the air pressure is increased to blow as much moisture as possible out of the cakes. Then the air is shut off and the press is opened. The cakes are now loosened by admitting air or steam to the bags. Cakes of three-quarters of an inch thickness or more will generally fall of their own weight; thinner cakes often need assistance with a paddle or an air or water hose. Very thin cakes, such as are met when clarifying sugar refinery liquors, are washed off automatically in the Sweetland filter by means of a special sluicing device.

Filtering and Washing

If the suspended solids are of uniform consistency and low specific weight no special effort is required to produce a uniform cake, but if the solids be of high specific weight, implying fast settling or a mixture of the two, it is advisable that a good circulation be maintained in the filter body throughout the whole filtration period. This will prevent the heavier particles separating from the lighter ones and settling to the bottom of the filter.

If the natural rate of filtration is not sufficient to produce this circulation a connection may always be made from the body of a leaf type filter back to the supply tank and sufficient sludge may be circulated in this manner to produce the desired results.

Continuous sampling of the effluent liquor will show that the specific gravity will not change materially until the bulk of the mother liquor has been forced out of the filter. Then it will fall very rapidly to 1 as the water washes out the remaining traces of liquor. If the gravity of the effluent wash water begins to fall at the start of the wash and continues to drop slowly it is a sign that the cakes were not properly formed or that they have been cracked or disturbed between the filtration and washing periods.

Complete washing generally requires a weight of water equal to from 85 to 125 per cent of the weight of the discharged cake, 100 per cent being considered very satisfactory.

Drying

Cakes formed of rigid noncompressible particles have drying limits which are governed by the physical qualities of the material rather than the type of filter used, but when the particles are soft and compressible it is to be expected that a plate and frame press will produce a more compact and drier cake than a leaf type filter.

Cleaning

Scraping the cakes off a filter cloth lying *against a plate or leaf* is to be avoided, for this not only wears the cloth but smears the cake into the pores as well.

Leaf type filters possess the advantage that the cloths can be inflated to loosen and discharge the cakes. This not only opens the pores and keeps the cloth free-filtering, but when scrapers are used it serves to raise the cloth from the frame so that it cannot be caught between the two. Certain salts do become precipitated in the fibers of the cloth as a result of the decrease in pressure from the filter body through the cloth to the atmosphere. These can generally be removed by filling the body with a dilute acid solution and allowing the filter to stand for an hour or so. It is not necessary to remove the frames from the filter for acid or soda washing.

American Continuous Vacuum Filter

The American Continuous Vacuum Filter is built up, first, of a hollow cast-iron shaft whose wall is thick enough to accommodate suitable cored longitudinal filtrate passages. These passages are closed at one end and terminate in individual ports in the casing of the rotary control valve at the other end. They have ports drilled along their length to correspond with the position of and to form the outlets from the filter leaves.

The sector-shaped leaves are constructed to stand compression and form a complete disk when inserted in place about the shaft. They are held in place by series of steel tension spokes, radiating between them from the center shaft, which are provided with clamps and tightening nuts on the end. Drawing up these nuts tightens the clamps which hold the sectors in place and presses the outlet nipples at the inner end of the sectors down tight against the gaskets in the ports of the shaft. This construction makes a very rigid disk and at the same time a very direct leak-proof connection from the sectors to the rotary control valve. The whole is supported in bearings over a suitable semi-circular pan containing the sludge, which pan is cut back on one side between each disk so as to allow the dry cakes discharged therefrom to fall direct to a receptacle beneath the filter. A valuable feature of this construction is that if the filter should be found to be too large, or if it should become necessary to run the plant at a reduced capacity, one or more disks may be removed, the ports in the shaft plugged up and the corresponding part of the pan temporarily filled in.

CAKE DISCHARGERS—Two types of cake dischargers are used. The first, a sheet metal deflector, is recommended for comparatively thick cakes which loosen from all but the center of the inflated bags. These are set so as to clear the frame proper by a half an inch and to just pass under the edges of the loosened cakes and strip them off. The second consists of a series of rollers and is recommended for thinner cakes of a slimy nature. The rollers are set to clear the frames and the bags are inflated so as to press the cakes out against them. The loosened cakes adhere to the rollers and are carried to a scraper set on the opposite side which discharges them to the hopper below.

ROTARY VALVE—The plug of the rotary valve has a tapered seat ground to fit the casing and is held tight in place by an adjustable spring. It requires very little attention as the spring takes up the little wear that may occur. It is provided with four parts and is held stationary while the machine revolves so that each port in the plug functions with those in the casing in their turn. The first is a high vacuum port connecting with all the filter leaf sectors which are completely submerged in the sludge, thus drawing the solution through the filter leaves and causing the cakes to be formed. The second, a vacuum port, connects with those sectors which have just emerged from the sludge and on which the cakes require washing and drying. The third is a compressed air port to inflate the bags as they approach the dischargers, and the last is an exhaust port to release the entrained compressed air as the sectors again submerge, thus reducing the work of the vacuum pump.

WASHING DEVICE—The system of washing the solubles from the cakes which consists of a series of atomizers which maintain a thin layer of water on the exposed cake surface. The vacuum draws this water through the cake.

The advantages which recommend the leaf type of continuous vacuum filter are:

The great filter area per square foot of floor space.

The light weight per unit of filter area which reduces transportation and installation charges.

The continued high capacity due to the cloths being kept flexible and free filtering.

The simple and accessible construction.

The multiple disk construction which permits the reduction in capacity by cutting out one or more disks.

The sectors can be changed readily.

The extremely dry cake discharged. Note: Owing to the excellent drainage from the bottom of the sectors during the drying position no moisture is blown back during the cake discharge.

The low maintenance costs. Every part that is subject to wear can be easily replaced.

Operation

The suction necessary to produce filtration is generally obtained by means of a dry vacuum pump. The filtrate and air drawn from the filter are received in a steel vacuum tank from which a centrifugal pump removes the filtrate from the bottom while the vacuum pump sucks the air from the top.

The filter pan is first filled with sludge, some means of maintaining a constant level in the filter being employed, such as a float regulating valve or an overflow. Then the filter is started turning, after which the vacuum and centrifugal pumps are started. It is sometimes best when starting to keep the drying and inflation ports closed until one revolution has been completed and a cake built on all the sectors, for if the drying port were open when there was no cake on the exposed surface it would be difficult to pull a good filtering vacuum.

Vacuum filters generally operate at a speed of from 2 to 12 min. per revolution, depending upon the filtering quality of the material. Six minutes is a good average speed.

Field of Usefulness of Each Filter

In general the Kelly may be said to be suitable for the filtration of sludges containing from less than 1 per cent of suspended solids to those containing the highest percentage of solids which can be conveniently pumped to and drained from the filter, wherein it may or may not be required to wash the cakes free from solubles with water, a solvent solution or a chemical reagent, and then to force as much excess moisture from them as possible by the use of compressed air or steam, and wherein in every case it is practical to build a cake of greater than one-quarter inch thickness.

The Sweetland filter will satisfactorily handle the same problems as the Kelly and in addition is to be recommended for the clarification of free-filtering or viscous solutions containing such a small percentage of finely suspended colloidal or gummy solids that it becomes necessary to add a small amount of kieselguhr or some other filter aid to the solution. As each leaf in this filter discharges into a common closed manifold pipe it finds a wide application in those industries where the cakes must be washed with a volatile solvent. When equipped with monel metal filter cloth this filter is used for filtration of caustic liquors directly after the causticizing reaction has been completed, and also for the removal of fuller's earth from vegetable oils after bleaching.

The Continuous Vacuum Filter is to be recommended for sludges containing over 10 per cent of comparatively free-filtering solids wherein a cake of greater than one-quarter inch thickness may be built with vacuum in from 1 to 8 min. Thinner cakes can be handled, but in most cases a thin cake indicates that the sludge builds too impervious a cake to allow efficient filtration under vacuum or that the percentage of solids in the sludge is too low.

The cakes may be washed by continuing the vacuum as the sectors emerge from the sludge and applying water to the exposed cake surface in the form of a very fine mist by means of spray nozzles. The cakes may then be air-dried by continuing the vacuum after the sectors have passed through the washing zone until it becomes necessary to cut off the vacuum and admit compressed air for the discharge. As the time of washing is restricted to a certain part of the revolution, cakes containing a high precentage of solubles cannot be completely washed in one cycle and must be puddled with water and refiltered. For such materials it may be better to use a pressure filter.

This filter is favored to two classes of products: slimy or sticky materials which tend to clog up the filter bags rapidly, and the heavy fast-settling materials which are difficult to keep in suspension. In the first case the inflation stretches out the bags each revolution and keeps them soft and free-filtering, while in the latter case a rapid circulation can be maintained by feeding in at the bottom of the filter midway between the disks and overflowing at the top.

In view of the fact that continuous vacuum filters cannot cover the wide field that pressure filters are adapted to and are to be recommended for only certain problems it is quite safe to say that their capacity will lie between the limits of from 300 to 700 lbs. of dry solids per sq. ft. of filter area per 24-hr. day. Capacities as low as 100 lbs. and as high as 2000 lbs. have been noted but these are unusual.

Labor Requirements

KELLY AND SWEETLAND FILTERS—When the filter station has been properly laid out for convenient operation one man can take care of from three to six filters. It takes one man from 6 min. to open the filter, dump the cake, and close it again ready for the next cycle when handling a heavy relatively dry cake which will fall of its own weight when the bags are inflated, to 25 min. for those viscous cakes which must be scraped off by hand or otherwise removed.

In the case of Sweetland sugar refinery filters wherein the thin cakes are sluiced off, the clothes can be washed clean in from 6 to 12 min. Automatic devices have been developed to drive the sluicing mechanism and when these are used one man can tend to as many as eight to ten filters.

AMERICAN CONTINUOUS VACUUM FILTERS—When these filters are properly installed there is very little for the operator to do after starting them up save to oil the bearings and keep an occasional eye on his vacuum and pressure gages. One man may tend to from one to ten filters.

Power Consumption

KELLY OR SWEETLAND FILTERS—The items of accessory equipment which consume power are as follows:

1—*Main feed pump or monte-jus supplying the filter*—A pump should be chosen, preferably a single stage centrifugal, capable of delivering the average volume of sludge to be filtered per minute at a pressure of 50 lbs. per sq. in.

2—*Wash water pump*—If the local plant supply pressure is not satisfactory. A pump of about half the capacity of the sludge pump should be chosen. It should be able to deliver this capacity at 50 lbs. pressure.

3—*Air compressor* To furnish air for drying the cakes and also to facilitate draining the excess sludge and wash water. The air compressor should have a capacity of from 12 to 30 cu. ft. of free air per square foot of filter area during the filtering period compressed to 50 lbs. pressure.

4—*Steam*—If found advisable in place of compressed air.

5—*Compressed air or water*—Where power devices are used for closing the filter (requirements very small).

6—When Sweetland filter cakes are to be discharged by means of the sluicing device a supply of 3.5 gal. of hot water per leaf per min. will be required at 75 lbs. pressure for a period of from 6 to 12 min.

AMERICAN CONTINUOUS VACUUM FILTER—The chief items for the Continuous Vacuum Filter are:

1—*Main dry vacuum pump*—This should have a displacement of from 0.6 to 1.25 cu. ft. of free air per sq. ft. of filter area per min.

2—*Compressed air*—To inflate the bags as they approach the scrapers. The air compressor should have a capacity of approximately 0.08 cu. ft. of free air per min. per sq. ft. of filter area compressed to 2 lbs. pressure.

3—*Power to drive filter*—The power required to start the filter will be about 0.005 h. p. per sq. ft. of filter area but once it is in motion the power consumption will drop to one-half this figure.

4—*Centrifugal pump*—In cases where there is not a sufficient drop below the filter to employ a barometric leg to remove the filtrate from the vacuum receiver and a centrifugal pump must be employed for this purpose, there will be an additional power consumption but it can be stated that the total power consumption for all of the above items should not exceed 0.06 h. p. per sq. ft. of filter area when starting up and approximately one-half of this when in continuous operation. These figures are based on a speed of from 6 to 8 min. per revolution.

Many people will instal an expensive high duty filter and then limit its capacity and usefulness by using an inadequate pump or other piece of accessory equipment. This procedure is to be strongly deprecated.

Filter Cloth Consumption

The saving in the filter cloth costs is one of the important items affecting the decision in favor of the leaf type filters. The cloth in a plate and frame filter serves not only as the filtering medium but also as the gasket between adjoining plates and frames. The cloths in a leaf type filter are freed from this gasket duty and therefore show a much longer life. A lighter cloth can also be used. Savings of over 50 per cent in the cloth bills are quite common.

Oliver Continuous Filters

By H. A. Morrison

Oliver Continuous Filter Co., 33 West 42nd St., New York, N. Y.

Different types of Oliver Continuous Filters are manufactured for various purposes:

STANDARD—For materials that do not attack wood, iron or steel. The tank is usually of steel, though redwood, pine or cypress may be substituted. Iron vacuum pipe, copper, steel or wood screen and cotton or wool filter cloth are used.

CAUSTIC—For all concentrations of caustic solutions. Cast iron and steel are employed throughout, but the latter is to be preferred by reason of lighter weight. Cotton cloth is used on very weak caustic (2 per cent or less), but woven monel metal cloth is entirely satisfactory and remarkably resistant to any strength of caustic, and is in general use in the stronger solutions. Caustic filters are provided with wash apparatus and are arranged to separate the filtrate into either two or three fractions as desired. The separation is made entirely automatic without unduly complicating the unit.

CAST IRON—For products such as sodium bicarbonate and ammonium nitrate, which attack steel. They are built with oscillating agitator only and the filter tanks may be jacketed for steam heating.

ACID RESISTING—For handling acid or corrosive solutions, built to secure maximum resistance to corrosion compatible with mechanical strength. The tanks are built of redwood, lead, copper, monel or rubber-lined steel, reinforced with lead covered rods. All parts of drum in contact with sludge are of wood and have ends enclosed in wood, lead or monel. Vacuum pipes are of lead, copper, monel or hard rubber. Screens of wood, lead, copper, bronze, monel or rubber coated metal support the filter medium, which may be cotton, wool, woven monel, spun glass or asbestos. Copper, phosphor bronze, silicon bronze or monel wire winding is used. Automatic filter valves are of bronze, antimonial lead, monel, aluminium or rubber. Special machines, such as an all-monel type, are built to meet unusual conditions.

Principles Involved

The underlying principle upon which the success of this filter rests is that of forming a comparatively thin cake (averaging 0.5 in.), followed by rapid washing and drying; and automatically effecting a complete discharge of this cake with a thorough cleansing of the filter medium after each cycle. Careful regard must be given the following points, if the drum filter is to take its rightful place in technical operations:

1—Maximum capacity is secured by building a cake that is just sufficiently thick to be discharged easily. However, dryness of cake or thoroughness of wash are frequently the determining factors as to speed.

2—The sludge to be filtered must be kept homogeneous by suitable agitation so that solids will not settle.

3—Pulp level must be maintained constant in the filter tank.

4—Excessive cracking of cake due to shrinkage must be prevented by even distribution of wash water, or by use of canvas drag or flapper, regulation of vacuum, etc.

5—Vacuum best suited to material being handled must be maintained. Frequently lower vacuum is maintained on the submerged portion of the drum than is carried on the washing and drying portions of the cycle, or vice versa, in order to secure proper ratio between thickness of cake and quantity of wash water or drying time.

6—Uniform conditions of concentration, temperature, and rate of flow must be maintained to secure maximum efficiency.

7—Automatic discharge of cake by means of low pressure air or steam or both will perfectly clean the filter medium each time a section is discharged. If patches are allowed to remain on the cloth, capacity will decrease, washing efficiency will fall, and cake moistures will increase. The success of the continuous wire wound drum filter has hinged largely upon this feature.

Uses

Granular, finely divided solids suspended in cold water with cake-forming solids amounting to 15 to 25 per cent of the weight of the mixtures constitute ideal feed for this filter. Cornstarch is an excellent example, and finely ground, clean quartz ore is another.

The filter is in no sense restricted to ideal conditions. Among the more important commercial uses may be mentioned ores and ore concentrates, pulverized coal, foodstuffs including beet sugar, cornstarch and glucose, heavy chemicals such as phosphoric acid and caustic soda, wood pulp in paper manufacture, aniline and other dyes and intermediates, notably β-naphthol and H-acid, edible oils such as cottonseed and coconut, lubricating and fuel oils, explosives including guncotton, and many others. Pineapple and other fruit juices are being clarified.

No one can decide by superficial examination whether or not a given filtration can be successfully made on this machine, unless identical material is already being satisfactorily handled. Careful and comprehensive testing is essential with particular attention to temperature, proportion of suspended or cake-forming solids, permeability of cake, chemical composition of solution, specific gravity of both solids and liquid, and extent of cake cracking while drying under vacuum.

The use of two filters in tandem for recovery of caustic from lime mud is coming to be regarded as standard practice. Double filtration takes advantage of countercurrent washing as effecting marked economy in wash water volume, with consequent increased concentration in the resulting filtrate.

Clarification of glucose sirup is interesting because in this case a very slight percentage (about 0.35 per cent) of cooked gluten is removed from 18° Bé. glucose at a temperature only slightly below the boiling point (190° F.). An inert material, possessing good filtration characteristics, is automatically added to the glucose as it enters the filter. This increases the permeability of the gluten cake enormously. Repulping and constant return of all but 1 per cent of the cake being discharged, maintains the proper density in the filter tank at all times and permits high capacity in terms of filtrate. Special filters having 60 to 70 per cent of the cloth constantly submerged have been developed for glucose filtration.

Vegetable carbons are gaining ground against bone-black for decolorizing sugar juices, and the necessary agitation and contact are best secured on a series of continuous filters. Countercurrent methods are used here and the carbon travels through the system in a direction opposite to that taken by the juice. This results in enormous reduction in the amount of carbon locked up in process and greatly reduces floor space required.

Washing of wood pulp for recovery of cook liquor has only recently been perfected on a working scale. This application now bids fair to become the most notable improvement in the paper industry during recent years.

It is frequently contended that continuous filters sometimes fail to make a clean filtrate. Proper choice of filter medium, reduction of vacuum during the early stage of cake building, and careful regulation of air or steam pressure while discharging cake, all assist toward producing clean filtrates.

Regulation of vacuum on different portions of the cycle provides flexibility and ease of adjustment to suit changing conditions. Both gypsum in acid solutions and lime carbonate in caustic solutions build cake rapidly, and thickness of cake must be regulated by decreasing vacuum on the cake-forming portion of the cycle in order that washing and drying may proceed under the high vacuum essential to best results.

From a cake-forming standpoint, the filtration of gluten presents the reverse case since high vacuum on the submerged portion of the cloth makes the first portion of cake extremely compact, thus reducing capacity.

The filtration of cold saccharate of lime is in strong contrast also, since high vacuum (24 in.) is used on "pick up" or cake-forming period in order to form cake of maximum thickness, whereas vacuum is reduced on portion of drum above pulp level in order to prevent cracking of the extremely delicate cake of trisaccharate of lime which washes rapidly under low vacuum.

ADVANTAGES

1—Continuous and automatic—no break in the cycle of formation, washing, drying, and discharge of cake.

2—All stages under constant observation.

3—Flexibility of adjustment permits handling products of widely divergent nature by changes in (*a*) cloth, (*b*) drum speed, (*c*) percentage of submergence, (*d*) regulation of vacuum, (*e*) position of blow, (*f*) temperature of feed.

4—Results uniform under any given conditions.

5—Less wash water needed to secure high purity in material being washed.

6—Personal factor largely eliminated.

7—Economy of floor space.

8—Power input is small per unit of work accomplished.

9—Saving in filter cloth.

10—Reduction in labor.

LIMITATIONS

1—Will not remove liquid contained or absorbed inside the individual particles of solids being filtered. Such materials cannot be filtered but must be pressed or squeezed to remove the contained liquid.

2—Finely divided solids of colloidal nature, especially when contained in relatively large volumes of liquor, must be thickened before filtration.

3—Cannot handle products that form explosive or inflammable gases under vacuum.

4—Structurally unsuited to handle the stronger acids—hydrochloric, nitric, hydrofluoric, etc.

5—Cannot operate at temperatures above 200° F.

6—Unsuited for dewatering products that form an extremely impervious cake, except when admixture of inert filter aids, such as silica, sawdust, fine coal, calcined clay, etc., is permissible.

The Atkins-Shriver Automatic Filter Press

By H. D. Atkins

T. Shriver & Co., Hamilton St., Harrison, N. J.

The automatic filter press is a modified form of the circular center feed press. The automatic feature lies in the method provided for removing the cake. This consists of a number of plows corresponding to the number of filtering chambers, fastened to a shaft passing through the center opening in the plates. This shaft is carried in bearings mounted near the outer edge of hubs which are fitted into bearings in the head and follower.

The center openings in the plates are large enough to receive the plows and shaft assembled as a unit, and at the same time to permit the cake to drop through the same opening by gravity as it is removed from the chambers by the plows. The hub that is mounted in the follower has an opening through its center to permit the passage of the cake from the press.

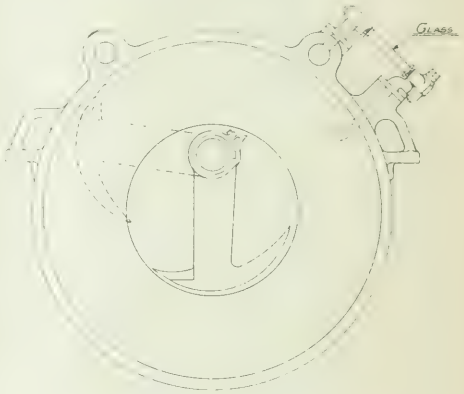
The filtering unit is arranged to swing on trunions having bearings in the leg supports. This permits swinging the unit to horizontal position for dressing, cleaning, and making repairs, and to vertical position while the press is in operation.

The press is fed at the bottom and the cake is delivered through the opening in the hub mounted in the follower. These openings are controlled by valves.

Power is applied through appropriate gear trains to the plow shaft for actuating the plows, to the hubs for actuating these parts as a function of the dumping operation and for the regulated feed of the plows through the cake.

OPERATION

The material to be filtered is delivered to the press by pump, monte-jus, or gravity, until a full cake is formed. The cake is washed or blown by switching the connection to the medium to be used for this purpose. The valve controlling the delivery of the cake from the press is now opened and power is applied to the hubs and plow shaft.



ATKINS-SHRIVER PLATE AND PLOW ARRANGEMENT

Inasmuch as the bearings for the plow shaft are located near the outer circumference of the hubs, the shaft is carried bodily around the opening in the plates while the plows are moved in an expanding spiral. The points of the plows move gradually into the chambers, cutting a uniformly thick slice from the cake until the entire chamber is cleared, except for a thin layer that is left on the cloths. The leading faces of the plows direct the layers of cake removed to the center opening through which it falls out of the press.

During the pumping operation the plows travel through an arc of about 100° from their starting position within the center opening until they are returned to this position.

Upon completion of the dumping operation, the cycle of filtering and dumping is repeated without opening the plates and frames.

If the thin layer of cake left on the cloths by the clearance given the plows interferes with efficient filtering, this residue may be cleared off by water, air or steam, applied to the back of the cloths through appropriately arranged connections and parts. During this operation the plows may be moved into the chambers while the cloths are held away from the plates by the pressure. The cake thus removed may be directed back to the material being filtered.

The length of a cycle of operations depends upon whether the material being handled is free filtering, but this time may also be varied in the original design of the press by varying the depth of cut made by the plows and by regulating the thickness of the frames.

APPLICATION

The design and operation of the press are favorable to any free-filtering material that may be handled by any metal press. On account of the first cost of the press it should be employed in large units handling large tonnage.

ADVANTAGES

1—Automatic dumping without opening the press, thus avoiding the resultant wear and tear on clothes.

2—Labor saving. One man may handle a number of presses because the plates do not have to be handled or the press closed up after each cycle.

3—Thorough washing of cake on account of short travel of wash water to affect the whole body of the cake.

4—Washing filter cloths without removing them from the press.

5—Adaptability to material-handling arrangements to carry away the cake, owing to the restricted space within which the cake is delivered from the press.

Vallez Rotary Filter

By **H. A. Vallez**

205 Mountain St., Bay City, Michigan

The Vallez filter is made of a cast-iron cylinder, divided horizontally into two halves. Inspection doors are located on one side of the upper half, and on the top are placed spray pipes connected with water and compressed air, used for removing the cakes from the frames. The sprays are so located that each frame revolves between two of them, and the whole surface of the frames comes in contact with their action. The bottom of the lower half contains a right and left hand screw conveyor to discharge the cakes through a door situated in the middle and at the bottom. The bottom of the press is provided with a header connecting with it at four places, to insure a perfect distribution of the material to be filtered. This header also contains the necessary inlet and drainage valves and the steam valve used in washing cloths in the filter. A drainage valve is also provided at the very lowest point of the shell. The proper gears and driving pulleys to revolve the filtering element and the screw conveyor are placed at one end of the shell, and at the other end are located the outlet pipes and the valves for the filtered material, wash water, etc.

A cake indicator is provided in the middle of the shell. This indicator consists of a small paddle placed between two of the frames and resting on the surface of one of them. As the cake becomes thicker the paddle rises from the frame and moves an indicating needle mounted on a dial outside showing the thickness of the cake at all times.

The filtering element is composed of a series of frames mounted on a hollow shaft and spaced 2.5, 3, or 6 in. apart, according to the material to be filtered. These frames are held together by the coupling at each end of the shaft and are key-seated on the same. Four spacing bars hold the frames at equal distances from each other, and act as scrapers against the sides of the shell. Male and female couplings connect the filtering element with the driving shaft and outlet pipes.

The frames are made of two perforated metal plates, kept apart by a coarse screen. The hubs of the frames are provided with the proper openings to connect the inside of the frames with the hollow shaft. Filter cloths of any material can be used, depending upon the material to be filtered. They are fastened to each side of the frame with metallic rings.

The shaft upon which the frames are mounted is made of very heavy tubing and a key seat runs its full length. Proper openings conduct the inside of the shaft to the frames.

OPERATION

During the operation the filtering element revolves about 1.5 times a minute. The thickness of the cake formed varies, depending upon the material being filtered, and the frames are spaced on the shaft accordingly. The pressure upon which the filter operates also varies with the material.

The washing of the cakes can be accomplished by admitting water without removing the excess of liquid in the filter, or by removing this excess with compressed air before the water is admitted.

After the washing, the excess water is blown out with compressed air, steam or compressed air is passed through the cakes to dry them, and the cakes are loosened from the frames with water or compressed air, and discharged by the screw conveyor. The filter is then closed and ready for another operation.

The filter cloths need never be removed from the frames until worn out. To wash the cloths the filter is filled with water to within a few inches of the shaft and the washing chemical is added. The washing solution is boiled by means of the steam inlet provided for this purpose, and the filtering element is revolved so that the cloths are washed as in a laundry machine.

To facilitate the removal of the filtering element when the cloths must be changed, the filters are installed under a mono-rail trolley to which a chain fall or some other lifting device is attached. The upper half of the shell is removed and the couplings at the ends of the filtering element are disconnected. The filtering element can then be removed and a new element inserted in a very short time. In a large installation it is always advisable to have one or two extra filtering elements on hand to avoid placing the filter out of commission while the worn-out cloths are being replaced.

London Chemical Society's "Annual Reports" at a Reduced Rate

The Council of the London Chemical Society has expressed pleasure in meeting the wishes of the Council of the American Chemical Society by arranging again to supply copies of the "Annual Reports on the Progress of Chemistry" to members of our Society at a reduced rate. Any member of the American Chemical Society can obtain a copy of the 1921 Annual Reports by sending his order, accompanied by a remittance of 7 shillings (made payable to S. E. Carr) to the Assistant Secretary, Chemical Society, Burlington House, Piccadilly, London, W. 1, England. The 7 shillings covers postage. All orders must be in by January 1, 1922, as it is necessary for the London Chemical Society to know the number of copies desired in advance of publication. Each applicant should make known the fact that he is a member of the American Chemical Society.

Our gratitude is due the London Chemical Society for the spirit of coöperation which thus makes possible the wider distribution in the United States of these excellent critical reviews. They fill a need which a good many American chemists have felt.

To those not familiar with the Annual Reports, it is explained that they appear in the form of a book, well bound, which is divided into chapters relating to different branches of chemistry, each of which is written by a chemist of high standing. References to original papers are given, and author and subject indexes are provided. These reviews, since they furnish continuous reading and since they are of a critical nature, serve as a most interesting, convenient and valuable means by which one can refresh his memory or become informed as to the more important advances in chemistry during the period covered.

Technical Association of the Pulp and Paper Industry

The joint meeting of the T. A. P. P. I. with the American Pulp and Paper Mill Superintendents Association, scheduled to be held during the week of October 18, was cancelled, on account of the probable poor attendance and lack of enthusiasm consequent on the business depression. It is felt, however, that such a joint meeting should be held at some future date, and a motion to that effect has been adopted by the Executive Committee of the Technical Association of the Pulp and Paper Industry.

EMULSIFICATION SYMPOSIUM

Papers presented before the Section of Petroleum Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

Emulsions with Finely Divided Solids

By T. R. Briggs

Cornell University, Ithaca, New York

Pickering[1] was apparently the first to recognize clearly that finely divided solids are capable of acting as emulsifying agents. He wrote as follows:

> Apparently, a precipitate consisting of any insoluble substance which is wetted more easily by water than by oil, if in a sufficiently fine state of subdivision, will equally act as an emulsifier ***** and it is possible under the microscope to see the coating of solid particles which envelop the oil particles.

Pickering prepared emulsions of a petroleum oil in water with the aid of so-called basic copper sulfate and other precipitated finely divided solids. He showed that the drops of oil were kept from coalescing by being coated with a pellicle of the finely divided solid material. In all of his emulsions, however, oil formed the drops, and he did not complete his experiments by preparing emulsions in which the drops consisted of water, suspended in oil as the outside phase.

A few years later Newman,[2] at Bancroft's suggestion, showed that water may be emulsified in benzene by the use of magnesium or calcium oleate, and in this way called the attention of chemists to emulsions of the water-in-oil type, which, though long recognized by pharmacists, had more or less escaped consideration by others. Thereupon the work of Pickering with solid emulsifiers was continued by Schlaepfer,[3] who succeeded in obtaining emulsions of water in kerosene by the use of carbon black or soot as the emulsifying agent. As the result of these and other researches, it is now generally recognized that finely divided solids may play an important role in the formation and existence of many well-known emulsions, such as ready-mixed paints and crude petroleum.[4]

It is part of the purpose of this paper to emphasize the fact that emulsions with finely divided solids are essentially similar to those in which an apparently soluble emulsifier is used, such as sodium oleate or gum arabic. In every case, investigation has shown that the apparently soluble emulsifier is in colloidal suspension in the outside phase of the emulsion and therefore constitutes a third phase in the system, exactly as a solid emulsifier can be seen to constitute a third phase in such systems. Furthermore, it is accepted by nearly everybody that the globules of liquid in all ordinary[5] emulsions are invariably coated by some kind of film or pellicle[6] which tends to prevent coalescence, and that this film or pellicle is present whether the emulsifier is apparently soluble or consists of a finely divided solid. In view of the vast majority of the experimental evidence, it seems safe to assume that the presence of a film of emulsifying agent is absolutely essential to the existence of all ordinary emulsions.

The discussion being limited for the moment to finely divided solids or to their suspensions as emulsifying agents, one may ask how the necessary interfacial films are produced. Separation and concentration of finely divided solid, such as hydrous oxide of iron, at the interface between benzene and water, for instance, can scarcely be due to a lowering of the interfacial tension, for hydrous iron oxide does not affect the surface tension of water. For all those cases, therefore, in which the interfacial solid is known not to affect the interfacial tension, it seems necessary to postulate that the solid is wetted to some extent by both liquids comprising the emulsion.[1] This must be done in the case of the solid emulsifiers studied by Pickering, and possibly also in the case of saponin and gum arabic which have relatively little effect on the surface tension of water.

The next question which arises is in regard to the type of emulsion—oil-in-water or water-in-oil—that may be formed through the agency of an interfacial, finely divided solid. It is generally agreed that the liquid which wets the solid emulsifier the more strongly under the conditions of the experiment, tends to become the outside phase, the less strongly wetting liquid being broken up into drops. Just why this is so is difficult to explain satisfactorily for the moment.

It was pointed out in a previous paragraph that a finely divided solid can serve as an emulsifying agent only if it possesses the power to separate out or concentrate at the interface between the two liquids. At the same time it must be capable of forming a film which is sufficiently continuous and elastic; to do this the solid particles apparently should be extremely minute, as Pickering has stated in the paragraph quoted previously. Hence it follows that influences opposing separation of the solid at the interface or increasing the size of the individual particles which do pass into the interface, will tend to prevent the formation of a stable emulsion.

The process of interfacial concentration may be looked upon as a process of distribution of finely divided solid between the interface and one at least of the component liquids. Anything therefore which carries the solid particles into one liquid must tend to remove them from the interface. Hence a peptizing agent tending to carry the solid into suspension in one of the liquids will make the solid less interfacial, other things being equal, and will oppose the formation of an emulsion. For instance, Reinders[2] found that gold separated out as a semi-metallic, interfacial film, blue by transmitted and gold by reflected light, when a gold hydrosol was shaken with isobutyl alcohol. On adding to the gold hydrosol gum arabic as peptizing colloid, however, metallic gold no longer passed into the interface with isobutyl alcohol. Further evidence bearing directly on emulsions will be offered in experiments shortly to be described.

On the other hand, if a solid is already in suspension in one of the liquid emulsion components and is prevented from being sufficiently interfacial because of strong peptization, it ought to be possible, by adding a flocculating agent, to counteract the peptizing influence and to force the solid into the interface. There should result accordingly an increase in the emulsifying action of the solid material. This is often the case in practice as the experiments to be described indicate. If, however, a very powerful flocculating agent is used, the finely divided solid may be caused to agglomerate into large masses or flocks, so rendering the formation of a suitable emulsion film impossible. It thus follows that if an aqueous suspension of a solid is used to emulsify oil in water, a substance having a weak flocculating effect on the suspension may be expected to help in the emulsifying process, while a powerful flocculating agent will be harmful. Experiment has confirmed this expectation.

---

[1] *J. Chem. Soc.*, **91** (1907), 2001.

[2] *J. Phys. Chem.*, **18** (1914), 34.

[3] *J. Chem. Soc.*, **113** (1918), 522; *cf.* Moore, *J. Am. Chem. Soc.*, **41** (1919), 940.

[4] Padgett, *Chem. Met. Eng.*, **25** (1921), 189.

[5] Excepting possibly suspensions of liquid-in-liquid in which electrical peptization is brought about by the adsorption of ions. Ellis, *Z. phys. Chem.*, **80** (1912), 597; Powis, *Ibid.*, **89** (1914), 91, 179.

[6] Briggs, *J. Phys. Chem.*, **19** (1915), 210.

[1] Hofmann, *Z. phys. Chem.*, **83** (1913), 385; Reinders, *Z. Kolloidchem.*, **13** (1913), 235; Bancroft, *J. Phys. Chem.*, **19** (1915), 286, 513.

[2] *Loc. cit.*

EMULSIONS WITH HYDROUS FERRIC OXIDE

A suspension of hydrous ferric oxide was prepared by adding crystalline ferric chloride to boiling water and submitting the suspension to partial purification by dialysis in collodion sacs. The suspension contained approximately 10 g. of oxide per liter. Forty cc. of this nearly clear suspension were shaken in a bottle with 10 cc. of benzene, but no emulsion was produced, the benzene and water separating into two continuous layers shortly after shaking ceased. When, however, 1 g. of sodium chloride (free from sulfates) was added to the oxide suspension and the latter was shaken anew with benzene, a coarse, unstable emulsion of benzene in water was produced. As the concentration of salt was increased in the oxide suspension, the stability and the degree of dispersion of the emulsified benzene were greatly enhanced, fairly permanent emulsions being ultimately obtained. In time the emulsified benzene floated to the top of the water layer in the form of a brownish yellow cream and carried with it a large proportion of the oxide originally suspended in the aqueous phase. To make certain that the sodium chloride itself contained no emulsifying impurity, a blank experiment was carried out by shaking benzene with solutions of the salt; but no trace of emulsion-building was observed in any case. When kerosene was substituted for benzene, similar results were obtained.

These experiments indicate that sodium chloride, a weak flocculating agent, drives ferric oxide out of suspension in water or at least destabilizes the suspension, and forces the oxide into the interface. By doing so, it causes the oxide to act as an emulsifying agent. That weak flocculation does actually occur is evident by inspection, for the suspension becomes noticeably more turbid on the addition of salt and settles out after a considerable interval of time.

Barium chloride, also a weak flocculating agent toward the suspension of ferric oxide, acted quite as sodium chloride did in bringing about emulsification. But when sodium sulfate, a powerful flocculating agent, was added, no emulsions were produced, the ferric oxide being precipitated in flocks which were too coarse in size to form a suitable emulsifying film.

EMULSIONS WITH ARSENIOUS SULFIDE

Six grams of arsenious oxide were dissolved in water and the solution was treated with washed hydrogen sulfide. The filtered suspension of the trisulfide was purified partly by dialysis and was diluted to 600 cc. Forty cc. of the yellow suspension were shaken with 10 cc. of benzene, and, as was the case with the iron oxide suspension, no benzene was emulsified. On adding sodium chloride, however, emulsions of benzene in the aqueous phase were obtained on shaking, exactly as in the previous work. Experiment showed that 0.16 g. of sodium chloride added to 40 cc. of the sulfide suspension was sufficient to cause the complete emulsification of 10 cc. of benzene. This quantity of salt was observed slightly to coagulate 40 cc. of the suspension after an hour. It was apparent, too, that the sulfide became strongly interfacial as salt was introduced and emulsions were obtained, for the drops of benzene could be seen to carry a yellow film, and much of the sulfide was floated up.

When large amounts of salt were used the emulsions became less complete and coarser, although the sulfide became increasingly interfacial. Evidently flocculation had gone too far, and the solid was no longer able to form about the benzene a suitably fine-grained film. For the same reason barium chloride, a strong flocculating agent analogous to sodium sulfate with ferric oxide, produced far less stable and effective emulsions than sodium chloride did, when added to benzene and sulfide suspension. It is evident that the experiments with arsenious sulfide are quite in line with the experiments with ferric oxide, and that the two sets of experiments afford a striking confirmation of the theory.

ANTAGONISTIC SOLID EMULSIFIERS

It has been pointed out in a former paragraph that the two types of oil-and-water emulsions have now been prepared, not only with so-called soluble emulsifiers, but also with finely divided solids. Among the emulsifiers of the first class, sodium oleate produces emulsions of oil in water, while calcium oleate produces emulsions of water in oil (benzene). Clowes has shown[1] that if sodium oleate and calcium oleate are present in approximately equivalent quantities in a mixture of water and benzene, no emulsion at all is produced on shaking. That is, sodium oleate and calcium oleate are mutually antagonistic emulsifying agents, and when they are both present in the right proportions each neutralizes the emulsifying action of the other. Since among solid emulsifiers carbon black is known to emulsify water in oil while finely divided silica emulsifies oil in water, one should expect to find a similar antagonistic action between these two solids when they are used together. This was shown to be true in the following manner:

To 15 cc. of kerosene was added 0.8 g. of carbon black, which formed a black and fairly stable suspension in the oil. To this suspension in a bottle 25 cc. of water were introduced slowly and with shaking. In this way an emulsion of water in oil was formed, which mixed freely with fresh oil but did not do so with water. Finely pulverized silica which had been passed through a 350-mesh sieve was added to a second bottle containing the above-mentioned quantities of kerosene and carbon black, and water was introduced as before. It was found that the silica exerted a marked antagonistic effect on the carbon black, and rendered it much more difficult to emulsify the water. When the amount of silica exceeded 0.1 g. it was found impossible to emulsify any water at all, the mixture in the bottle separating after shaking into two sharply defined layers, an upper one of kerosene and carbon black and a lower one of water containing some silica in suspension. Likewise no emulsion was formed when equal parts of silica and carbon black were mixed.

On adding 15 cc. of kerosene to 25 cc. of water containing only pulverized silica, the oil was completely emulsified on shaking. Water was now the outside phase, for the emulsion mixed freely with water but not with oil. A small amount of carbon black added to the silica, however, sufficed to keep the oil from being emulsified, though unfortunately the quantity needed completely to prevent emulsification was not determined. A similar experiment was, however, carried out with kerosene, water, silica, and powdered mercuric iodide, the latter like carbon black being readily wetted by oil and tending to emulsify water in oil. It was found that approximately one part of mercuric iodide in 20 parts of silica was enough to prevent the latter from emulsifying 25 cc. of kerosene in 25 cc. of water.

SUMMARY

1—Emulsions with finely divided solids are similar to emulsions in which so-called soluble emulsifiers are used.

2—The general theory of solid emulsifiers has been reviewed and amplified.

3—It is absolutely necessary that the finely divided solids form a suitable film at the interface between the two liquids which are to be emulsified.

4—If the finely divided solid forms a stable suspension in one of the liquids, it may be necessary to add a weak flocculating agent before a satisfactory emulsion can be produced; but a powerful flocculating agent will usually prevent emulsification.

---

[1] *J. Phys. Chem.*, **20** (1916), 407.

5—Certain finely divided solids, such as carbon black and silica, are mutually antagonistic so far as the formation of emulsions is concerned, and in this respect are analogous to sodium and calcium oleates.

Emulsifying Agents in Oil-Field Emulsions

By J. L. Sherrick

Mellon Institute of Industrial Research, Pittsburgh, Pa.

Since publishing the results of a research on oil-field emulsions[1] carried on in the winter of 1918 to 1919, the writer has received many inquiries from widespread sources. Although the subject matter of the present contribution represents no additional laboratory research, certain points therein have been developed in discussion with associates and are offered in the hope that they will encourage further discussion.

Before considering the question as to the substance in crude oil which serves as the emulsifying agent, it is first necessary to review briefly the general conditions for emulsion formation.

Emulsifying Agents

The necessity for the presence of some third component to serve as an emulsifying agent has been recognized by almost all workers in emulsions. The substances, which function as emulsifiers, by collecting at the interface of the two liquids to form protective films for the dispersed phase are, however, quite varied in their nature.

The most common emulsifying agents are the emulsoid colloids like soap, gelatin, gums, starches, beeswax, etc. It seems certain also that *suspensoid* colloids may so serve, although they are not generally used. Pickering,[2] however, has gone a step beyond this and used finely divided solids for such a purpose. It has been claimed that ions adsorbed on the surface of liquid particles may serve as emulsifiers, and Ellis has prepared an emulsion which owes its stability to ion adsorption. It is probable, however, that for the formation of emulsions of relatively high concentration of dispersed phase, say 50 per cent or more, the presence of an emulsifier which will form a relatively tough and elastic film by collecting at the interface is necessary.

Types of Emulsions

Emulsions may be classified according to the position of the several phases. Thus we have oil-in-water emulsions, in which the oil is dispersed as small particles in a continuous water phase, and water-in-oil emulsions, in which the water is dispersed as small particles in a continuous oil phase.

The type of emulsion formed by any given oil with water depends primarily upon the nature of the emulsifying substance. Bancroft has explained this from the standpoint of surface tension. In a general way, however, the following applies: An oil-in-water emulsion is formed by the use of a water-soluble colloid as emulsifier; a water-in-oil emulsion is formed by the use of an oil-soluble colloid. With finely divided solid material, the liquid which more easily wets the solid material will be the continuous phase.

Oil-Field Emulsions

Oil-field emulsions belong to the water-in-oil type and as such must be formed by an oil-soluble colloid or a solid material more easily wetted by oil acting as emulsifier. The character of this emulsifier may most easily be shown by the actions of the emulsions under certain conditions of test.

It has been shown by the author that the water particles are negatively charged electrically, and indeed both alternating and direct current electrical treatment have been used to discharge these emulsions. As a matter of fact we have found that a static charge is sufficient to precipitate the water.

The water particles may be made to coalesce and precipitate by the addition of certain electrolytes, such as acids and iron salts. Such an effect may be due to the preferential adsorption of certain ions, but it is rather hard to believe that these emulsions, ranging from 10 to 60 per cent in content of dispersed water phase, owe their stability to ion adsorption alone. Even though Ellis has prepared emulsions stabilized by ion adsorption, these were extremely dilute emulsions and were of the oil-in-water type.

Certain water-soluble colloids, such as sodium oleate and the sodium salts of certain sulfonic acids render these emulsions unstable and precipitate the water if added in proper proportion. This is indeed what one might expect if the original emulsifying agent were an oil-soluble colloid as the action of two such colloids must be antagonistic, the one tending to form a water-in-oil and the other tending to form an oil-in-water emulsion. The precipitating colloid must, however, be added in exactly sufficient quantity to neutralize the effect of the original emulsifying colloid. If too large an excess is added it may bring about simply a phase reversal, changing the emulsion from the water-in-oil type to the oil-in-water type.

The action of certain organic solvents upon these emulsions probably throws more light on the nature of the emulsifying agent present than any of the other reactions. A standard method among oil men for determining the percentage of water in an emulsion consists in adding light gasolene to the emulsion and centrifuging the mixture when the amount of water in the sample can be read off from the graduated centrifuge glass. It has been found that ether serves even better than gasoline for this test.

The effect of these organic solvents in breaking the emulsions was thought to be due to the fact that the solvent mixing with the oil phase increased the difference in density of the two phases to such an extent that the emulsifier was no longer powerful enough to hold the emulsion. It was found, however, that a mixture of ether and carbon bisulfide of the same density as the emulsion served to break the emulsion more easily even than the light liquid ether.

The Emulsifying Agent

The substances, other than water and oil, present in these emulsions are the following:

Electrolytes in solution in the water phase.
Hydrated earthy material.
Heavy hydrocarbons, such as asphalt, asphaltenes, etc., probably present in colloidal solution in the oil.

The ions of the electrolytes present in the water phase probably affect both the magnitude and nature of the electric charge on the water particles but, as previously stated, it is rather hard to see how they could stabilize such concentrated emulsions. Above all, it seems hardly likely that ions could stabilize a water-in-oil emulsion, even granting that they might be effective for an emulsion of the opposite type.

We would expect hydrated earthy matter to be wetted more easily by water than by oil and, if a colloid, to be water-soluble. We seem to recall, however, having read that precipitated hydrous ferric oxide would occlude or adsorb small amounts of oil or grease contained in the solution from which it was precipitated.

---

[1] This Journal, **12** (1920), 133.

[2] *J. Chem. Soc.*, **91** (1907), 2001.

There seems to be little doubt as to the fact that some of the asphalt-like bodies are present in crude oil as oil-soluble colloids. However, if such were effective as emulsifiers, it would seem that all of the asphalt base oils should emulsify very easily, but this is not the case.

It seems entirely probable, then, that the hydrated earthy material, adsorbing the heavy asphalt-like bodies of the crude oil in a manner similar to hydrous ferric oxide, becomes an oil-soluble colloid, and as such forms tough elastic membranes about the drops of water. Richardson[1] has found such an oil-soluble colloid in Trinidad asphalt and has even reproduced such a colloid by mixing a water solution of colloidal clay with asphalts and asphalt oils and driving off most of the water with heat. It is probable that some such process took place during the formation of the crude petroleums, leaving them charged with such an oil-soluble colloid which later served as an emulsifier when the crude came in contact with water under conditions favorable for emulsion formation. Since the earthy material is an oil-soluble colloid in virtue of the fact that it carries adsorbed asphalt, when such asphalt is removed by organic solvents, the earthy matter is no longer oil-soluble and cannot therefore protect a water-in-oil emulsion.

In June 1918 the writer went from Houston up into northern Texas to investigate some "bottom settlings" which resisted an electrical treatment that was at the time very successful in breaking oil-field emulsions. This material which represented sedimentary accumulations from pipe line storage tanks was stiff and very sticky. It would not respond to electric treatment except when it was diluted with more than an equal quantity of good crude oil. Evidently the crude oil phase was much more firmly held in this emulsion than in those occurring in the oil fields but even it responded to organic solvents. This "B. S." contained about 50 or 60 per cent water, but was much stiffer than the regular oil-field emulsions containing a like percentage of water. It would readily serve to emulsify a clean crude oil with water and seemed to represent exactly such an emulsifier as we have assumed to be responsible for the formation of emulsions in the oil fields.

Common Characteristics of Crude Petroleum Emulsions

By E. E. Ayres, Jr.

Sharples Specialty Co., Philadelphia, Pa.

What do we mean by the "resolution of emulsions?" The man in the field who is responsible for production of crude petroleum considers his emulsion resolved when the water globules have settled, leaving the bulk of his oil homogeneous. The research chemist is often content with a proper degree of coalescence, for with the globules large enough, subsidence may be taken for granted.

Subsidence and coalescence should be regarded as of equal importance, for subsidence unaided may be too slow, and must leave an incomplete resolution in any case, while a coalescence technique which would leave the settling of the water beyond doubt might be too costly. Except with the least stable of emulsions, centrifugal engineers have found it profitable (usually by a correct use of heat) to increase the average size of the water globules before attempting centrifugal subsidence. The people who have been interested in commercializing the use of reagents and electricity for crude petroleum emulsions have found it necessary to facilitate (usually by an efficient gravity system) the settling that must, of course, follow coalescence to yield a practical resolution.

Gravity and Centrifugal Subsidence

Really efficient gravity systems are rare. Throughout the Middle West there are expensive continuous-flow basins that violate the first principles of subsidence. Gravity costs nothing except time, and it is therefore used injudiciously for easily accomplished subsidence, and is discarded as useless when the elapsed time seems too great. A few years ago centrifugal force was squandered in like manner. But centrifugal force is expensive, and centrifugal engineers were compelled to look for the fundamental principles which must be obeyed. The modern centrifuge probably secures as efficient subsidence as the mechanical limitations of the machine permit.

Factors Involved in Subsidence

Centrifugal and gravity subsidence are dependent, of course, upon differences in specific gravities. It is natural, therefore, that our first question should be "Is the absolute density of the suspended particle great enough for separation?" The answer is "yes" in every case. If we were to find a case in which the gravity of crude petroleum were exactly the same as the gravity of the suspended water, the equality could not exist at all temperatures because of differences in coefficients of expansion. An inspection of the form of Stokes' law which controls the motion of such particles will show the relative unimportance of absolute density. The centrifugal engineer considers two points: If the particle is too small, subsidence is impossible; if the viscosity of the continuous phase is too high, subsidence may be too slow.

In the case of crude petroleum emulsions the particles are never too small for subsidence. Viscosity varies widely, but not so widely as might be supposed. The extremely viscous emulsions so often encountered may comprise a continuous phase of low-viscosity oil, in which case subsidence will take place as readily as though the emulsion itself had a low viscosity. In other words, we may disregard the viscosity of the emulsion, and inquire only into the viscosity of the oil of the emulsion.

To get a clear idea of what gravity and centrifugal force will do to a crude petroleum emulsion let us consider a body of oil containing 15 per cent of water dispersed as small globules. If this oil is permitted to stand a sufficient time the emulsion will reach a state of equilibrium. The time will be dependent upon the size of the globules, the viscosity of the oil, and, in lesser degree, the difference between the specific gravity of the oil and the water.

At equilibrium, all of the globules of water, except a small percentage of the smallest, have settled to the bottom. The supernatant oil will therefore be reasonably free from water. Let us assume that one third of the settled globules are large enough to coalesce when brought into contact by subsidence. The coalesced globules will form a water layer at the bottom of the container. The other two thirds of the globules are too small for gravity coalescence, and remain as globules closely packed together in viscous formation. It is of interest that the highest centrifugal force will cause no greater degree of coalescence than gravity. The above example, if correct for a specific case of gravity separation, will apply with equal correctness to centrifugal separation. Furthermore, the small globules in the settled emulsion are packed into as small a space by gravity as they can be packed by the highest centrifugal force.

This indicates that the globules may be brought into contact by subsidence with relative ease. There are many emulsions that cannot be concentrated by gravity to contain more than 30 per cent of dispersed phase. The concentrated crude petroleum emulsions contain rarely more than 55 per cent water, which would indicate that the globules are of rather uniform size. Other much more stable emulsions can be concentrated by centrifugal subsidence to contain as high as 80 per cent of the dispersed phase.

---

[1] *J. Phys. Chem.*, **19** (1915), 246.

Emulsions containing only globules large enough for coalescence by contact at normal temperatures are infrequent.

Relative Time Required by Two Methods

The centrifuge has two related advantages over the gravity system. If the centrifugal force is from fifteen to eighteen thousand times as great as the force of gravity, the gravity separation will take fifteen to eighteen thousand times as long as the centrifugal. The emulsions in Kansas, Oklahoma, and some parts of Texas require the exertion of a force of this magnitude to effect subsidence in 1-in. layers, during a period of from 6 to 18 sec. The corresponding figures for gravity are from 24 hrs. to 3 days. The first figure conforms approximately to practice. The second figure is not easy to verify, because the more stable emulsions are centrifuged at high temperatures; and one rarely finds a tank of emulsion maintained for several days at high temperatures, except under conditions where evaporation losses of volatile fractions and the effects of severe convection currents interfere with subsidence.

The fact that the centrifuge cuts down the time required for complete subsidence means that an emulsion may be heated for this brief period at a permissible cost, and coalescence may be so greatly increased at the higher temperature as to yield all of the water as a homogeneous phase. Commercial centrifugal installations are invariably designed to secure this complete resolution either by heating the emulsion proper, or by centrifuging first at normal temperatures, heating the effluent concentrated emulsion to cause coalescence, and then recentrifuging the effluent emulsions. Occasionally it is necessary to use a more efficient coalescence method than heat.

Means of Producing Coalescence

HEAT—Heat, as a means for producing coalescence, is not always understood. A common mistake is to heat a petroleum emulsion by means of a closed pressure steam coil. The surface of the coil is above the boiling point of water. Globules of water coming in contact with this surface are vaporized and then almost immediately condensed by the cooler surrounding oil, resulting in the formation of globules smaller than those originally present. The usual practical effects of such heating are that (1) subsidence is aided because of lowered viscosity, and some water-free oil collects on the surface; (2) coalescence is retarded, and the settled emulsion (commonly called "cooked B. S.") is as difficult to resolve as any crude petroleum emulsion encountered.

A satisfactory method of inducing coalescence by heat is to have a live steam coil completely immersed in water in the bottom of a tank of emulsion. As the water heats, gentle convection currents are set up in the supernatant emulsion, and as the temperature of the emulsion rises some of the suspended water joins the water in the bottom of the tank, while the remaining suspended globules are large enough to respond easily to centrifugal force. Such a method is comparable with the heating of a beaker on a steam bath.

THE HATSCHEK FILTER—Heat is mentioned here because it is so generally employed. The next method is mentioned because it is so rarely employed and yet has such interesting possibilities. The term "filtration" has been used in four apparently distinct senses in current literature on colloids. The correct use of the word is for ultrafiltration—the passage of a liquid through a medium whose pores are small enough to retain the suspended colloid particles.

Hatschek devised his well-known filter of calcium carbonate to remove oil globules from water. The water passes through while the oil is retained, not because of the size of the pores, but because calcium carbonate is more easily wetted by water than by oil. Emulsions of the opposite type, like the crude petroleum emulsions, have been filtered in this way by using a medium more easily wetted by oil than by water, such as pulverized vulcanized rubber and iron sulfide. The method is not well adapted, however, to crude petroleum emulsions, because the retained globules do not coalesce by contact, and nothing is accomplished that cannot be accomplished by simple subsidence.

THE WETTED SEPTUM—Cottrell's "wetted septum," occasionally used in conjunction with the high voltage, crude petroleum emulsion dehydrators, has been termed a filter. This involves a principle opposite to that of Hatschek's filter. Cottrell uses a cellulosic medium (canvas) which is more easily wetted by water than by oil. The continuous oil passes through because of the large size of the pores. The dispersed water also passes through, but contact with the cellulose causes some coalescence. The objection to this device is that only the larger globules are coalesced, and the smaller globules form viscous clumps which soon close the pores of the canvas.

Inasmuch as the efficiency of the method depends not upon the size of the pores but merely upon contact, it would seem natural to replace the single layer of canvas by a thick bed of coarse granular material of suitable colloid properties. In the laboratory, excellent results have been secured by passing a crude petroleum emulsion through a column of granulated "vulcanized fiber." This material was chosen because it is cellulosic and yet will retain its physical form when water-soaked. The disadvantage of the nonporous vulcanized fiber is that the contact surface is not great compared with, for example, fuller's earth. The method is suggestive, especially with reference to those water-in-oil emulsions to which no foreign soluble substances may be added.

KIESELGUHR—The fourth use of the word "filtration" is in reference to a phenomenon which may not have been correctly interpreted. It is claimed that if a crude petroleum emulsion is passed through a bed of kieselguhr, the films around the globules of water are cut by the fine sharp edges of the medium and coalescence results.

The Use of Two Protective Colloids

One of the most interesting and practical ways of bringing about coalescence is that of pitting against each other protective colloids of opposite types—the hydrophile against the hydrophobe.

Presupposing a similar history, field emulsions as they occur with fresh water or salt water, hard water or soft water, sulfides or sulfates, contain globules of about the same average size. Naturally subsidence is no more difficult in one case than in another, being dependent merely upon the viscosity of the oil. Furthermore, the coalescence brought about by heat or by subsidence is so nearly the same as to show no difference in practice. By severe agitation, or by the blowing of live steam through a small nozzle, or by heating the emulsions in direct contact with surfaces above 100° C., the suspended globules of any crude petroleum emulsion may be broken down into smaller globules, so that subsidence and coalescence are both much more difficult. The size of the globule is dependent upon the history of the emulsion. But if we measure stability by the power of the hydrophobe to resist an opposing hydrophile colloid, emulsions of crude petroleum have a very low stability.

HYDROPHILE REAGENTS—The most commonly used reagent for "breaking" crude petroleum emulsions is water-soluble soap. The reason for the efficacy of soap is, of course, that water-soluble soap is a protective colloid of the type that stabilizes oil-in-water emulsions. If, in order to "break" an emulsion by this method, it is necessary to add a substance to the dispersed water, how can we hope to convey the substance through the enveloping oil? The wrong way would apparently be to agitate the petroleum emulsion with an aqueous solution of the substance (soap, for example). This procedure is often used and often gives good results, though it is not easy to understand what really happens. Any contact between the aqueous reagent, which by its character cannot be made to suspend in oil, with the water globules of the emulsion would seem to be fortuitous. However, such contact must take place in some instances.

The right way to use such substances as soap is to put the soap in such form that it is colloidally soluble in oil. One may prepare, for example, mixtures of sodium oleate with oleic acid, or mixtures of sodium resinate with free rosin that will go readily into apparent solution in the continuous oil. Contact with every water globule is in this way certain and coalescence is always immediate.

A concentrated solution of gelatin can be incorporated with fuel oil to produce "oil-soluble" gelatin. Starch is not regarded as a powerful protective colloid, but very small amounts added in proper oil-soluble form to crude petroleum emulsions will cause complete coalescence.

Nothing of value can be said in regard to the percentages of such hydrophile reagents required to "break" these emulsions, because, in practice, the effects of the reagents are progressive. Let us take, for example, an emulsion which can be separated in a given continuous centrifugal at the rate of 5 bbls. an hour. The addition of 0.001 per cent of oil-soluble sodium soap or glue or starch several hours before centrifuging will cause the rate of separation to be increased to 15 bbls. per hour. The same increase may be obtained by the addition of 0.01 per cent of hydrophile colloid 30 min. before centrifuging, or the addition of 0.1 per cent at the time of centrifuging. Within practical limits, the more reagent is used, the further will coalescence proceed in a given time. An absurdly small percentage of hydrophile is enough to insure complete coalescence by contact if the emulsion is given time to come to equilibrium.

Soap, glue, and starch may not be exactly compared in their action on crude petroleum emulsions for minimum percentages, because these minima are so low, but they appear to be practically equal in effectiveness when added, say, one hour before centrifuging. Likewise, crude petroleum emulsions of all sorts appear to be equally sensitive to these hydrophiles when used in the above manner. Whatever the stabilizing hydrophobe may be, it is of low power and present in all crudes in approximately the same amount.

If the hydrophobe is earthy material, the colloid particles are smaller than 1 μ. Of eighty-two samples of crude petroleum emulsions taken from the middle-western states, it was found that the earthy particles larger than 1 μ amounted to from 0.0005 to 0.2 per cent. The latter high figure applied only to old emulsion accumulations. It should be understood that reference is made only to emulsions in the field—not to the crude petroleum emulsions that accumulate in refineries where conditions are such that the solids content may be very high.

The determinations were made by centrifuging under such conditions that only particles larger than 1 μ were removed. The oil, after the removal of such particles, formed emulsions of the same stability as with the particles present.

Summary

It is all very well for the chemist to say that there are several perfectly satisfactory means for effecting coalescence and for increasing the rate of subsidence. That these ends may be invariably attained is indisputable, but there are engineering aspects of the practical problem that cannot be ignored. A beaker full of emulsion is easily handled. The labor costs of such handling are immense, but they are never figured. To translate a laboratory process to an oil field where thousands of barrels of emulsions must be taken care of to make room for other thousands of barrels is no small task.

A total of about 23,000 bbls. of crude petroleum emulsions are being handled per day in fifty-seven centrifugal plants. Every barrel could be resolved without the aid of centrifugal force—in some instances at lower cost, but the centrifuge offers an engineering solution to the problem. Is it more economical to employ a specialist engineer to adapt a theory of coalescence and subsidence to special conditions of volumes, location, etc., or to buy a plant "ready made," wherein problems of continuity and autonomy have been satisfactorily answered in terms of machine design? Many operators have taken neither course. They have, instead, left the solution in the hands of non-specialist engineers and executives and after many failures and extra appropriations have concluded that their particular crude petroleum emulsion is different from other crude petroleum emulsions. The conclusion is erroneous, of course, and in recent years we have heard such conclusions less frequently expressed than formerly.

Any crude petroleum emulsion can be resolved by means of centrifugal plants. The plants can be installed and put into operation in twenty-four hours. All that is required otherwise is to pipe the emulsion to the plant and to pipe away the separate oil and water. The variant is the rate at which a plant of a given size can handle a given emulsion, and the rate can be predicted with fair accuracy from data on the history of the emulsion (which determines the size of the particles) and the specific gravity of the oil (which is associated with viscosity).

Centrifugal results are uniform because the modus operandi is correctly understood. Some electrical processes have been notoriously limited to one particular field or to one kind of crude petroleum. Such limitations would not exist if the principles of the electrical processes were clear.

Furthermore, some chemical processes have been declared successful for this emulsion and unsuccessful for another. If such declarations have foundation, it is clear that the action of the chemical was accidental or that the reaction was unknown. That the oil-soluble hydrophile colloid should give the same coalescence to every sort of crude petroleum emulsion is evidence that the supporting theory is a correct one.

Crude petroleum emulsions, as they occur, are so much more uniform in properties than refinery emulsions, that the problem of their large-scale resolution is simple by comparison.

Oil Field Practice in Handling Crude Oil Emulsion

[ABSTRACT]

By Sidney Born

Transcontinental Oil Co., Muskogee, Oklahoma

The earliest method for removing emulsions from crude oil was to allow the oil to settle in a tank. The first forward step toward breaking up these emulsions was to expose the B. S. in large ponds to the heat of the sun. This process of "sunning" resulted in large evaporation losses, but it did succeed in breaking up part of the emulsion and the clear oil could be skimmed off the pond from time to time. From these crude methods, the steaming plant developed. This consists of a tank or battery of tanks in which the emulsified crude oil is heated with steam, raising it in temperature and breaking up the emulsion. The earlier steaming plants were frequently operated in such a manner that practically all of the gasoline and naphtha in the crude oil was lost.

THE MODERN STEAMING PLANT

There has been developed a modern plant which is to-day the most extensively used method of breaking up and settling B. S. The new type of plant generally consists of a battery of five tanks. In the first tank, or "gun barrel," the crude emulsified oil is heated with steam. Great care must be taken to heat the oil to the proper temperature and thermostatic control is maintained in the most modern types of plants. The best temperature for breaking up the emulsion will vary with the kind of crude and the nature of the emulsion. The temperatures range from 122° to 160° F. From the gun barrel tank, the oil generally overflows to a second tank in which it is further heated, and from this it overflows into a third tank in which any traces of emulsion that have not been removed are further broken up. From the third tank, the oil is allowed to overflow into storage tanks in which it is allowed to settle to remove any slight trace of B. S. or water. The process is continuous and is not interrupted for weeks or months. The salt water which accumulates in the gun barrel and other tanks is drawn off from time to time.

THE COTTRELL PROCESS

The Cottrell process is particularly adapted to heavy oils, such as Californian and Mexican crudes. The process consists in subjecting the oil, warmed to about 160°, to a high voltage current. Several installations have been made in the mid-continent field, but the high cost of electrical energy has held up the further use of the process.

CHEMICAL TREATMENT

Where large amounts of emulsified oil and B. S. are to be handled, chemical treatment is particularly suitable. A great many salts, alkalies, soaps, and other substances have been used for breaking up persistent emulsions. The successful application of chemical treatment depends not only on the chemicals used but on their concentration, the manner of application, and the apparatus employed.

CENTRIFUGAL METHODS

During the past two years, the use of the supercentrifuge has developed remarkably. This machine operates somewhat on the principle of the cream separator. It consists of a frame supporting a small high-speed steam turbine with a vertical shaft. The turbine has but one bearing, a cone resting on a set of ball bearings. The bowl or revolving member of the centrifuge has a diameter of about 4.5 in. and is suspended from the turbine by a vertical shaft or spindle. Power is thus transmitted directly to the bowl by the turbine. The bowl is made of special alloy steel and the bottom of it is provided with a boss which rotates within a drag bushing made of bakelite to keep the bowl in proper alignment. The bowl rotates at a speed of about 17,000 r. p. m. The advantage of this machine over the ordinary centrifuge lies not only in the increased speed but in the fact that the elongated bowl increases the time limit during which the centrifugal force acts on the particles under treatment.

In practice, the emulsified crude oil is generally pumped to an elevated storage tank at least 30 ft. above the centrifugal machine, from which the oil is fed to the machine by gravity. The oil is heated in these storage tanks to 110° to 180°, depending upon the character of the oil and the emulsion. In starting the machine, the bowl is set rotating slowly, and water is then admitted until the bowl has reached its full running speed. It is customary to employ salt water which has been separated from the oil for this purpose. After the machine reaches its full speed, the oil is gradually admitted until the machine reaches its full capacity. This can always be noted by watching the quality of the oil issuing from the machine. One stream consists of oil which is clean and the other of water and any unacted-upon emulsions. It is sometimes advantageous to add a small amount of free water to the oil to be treated. The capacity of this machine runs from 100 to 200 bbls. of finished oil per 24 hrs. Of course, in the case of very heavy emulsions, the capacity may be somewhat lower.

In a test installation, two 100-bbl. tanks were set upon a platform and connected with one supercentrifuge. There was also installed a small pump to pump the oil to the tanks, heating coils in the tanks, the necessary connections and other equipment necessary for a test run of 24 hrs.

The following table shows the result of this run.

		Incoming Oil		Treated Oil		
Hours	Temp. ° F.	B. S. Per cent	Water Per cent	B. S. Per cent	Water Per cent	Capacity Bbls. per Hr.
0	150	21.0	14.0	0.5	...	9.7
1	145	20.0	15.0	0.4	...	10.4
2	140	22.0	13.0	0.4	...	9.9
3	150	20.0	12.0	0.3	...	10.2
4	150	14.0	8.0	...	...	10.2
5	145	14.0	7.0	...	...	9.9
6	150	18.0	8.0	0.4	...	10.2
7	155	20.0	6.0	0.2	...	10.4
8	150	18.0	6.0	0.3	0.2	9.7
9	150	37.0	...	0.1	0.4	9.9
10	140	26.0	1.0	0.5	...	9.6
11	146	25.0	...	0.1	0.2	9.9
12	149	15.0	0.5	0.4	...	9.4
13	(Shut Down to Repair Pumps for 1.25 Hrs.)					
14	150	18.0	0.5	0.4	0.5	9.2
15	147	16.0	0.5	0.4	...	9.0
16	148	13.0	4.0	0.1	...	9.7
17	150	12.0	2.0	...	0.1	9.9
18	154	13.0	2.0	...	0.1	9.9
19	150	15.0	2.0	...	...	9.2
20	145	16.0	2.0	...	...	9.4
21	150	15.0	6.0	...	...	9.7
22	150	17.0	5.0	...	...	9.5
23	150	21.0	3.0	...	...	9.7
24	150	21.0	3.0	...	...	9.4
Average	148	18.9	4.8	0.19	0.06	9.8

The oil in question had an average B. S. content of 18.9 per cent and an average free-water content of 4.8 per cent. After treatment, the oil had an average B. S. content of 0.19 per cent and a free-water content of 0.06 per cent. This particular oil was heated to 148° F. before centrifuging, and the machine handled approximately 14 bbls. of wet oil per hr., and gave a yield of 9.8 bbls. of clean oil per hr. The operating cost will vary greatly, depending upon the size of the installation, the character of the oil, and other local conditions, but should not exceed 7 cents per bbl. of oil treated. Very heavy emulsions can be handled in these machines. The B. S. content can be reduced from as high as 70 to 80 per cent to as low as 0.5 per cent without any difficulty.

TOPPING PLANTS

Another method of breaking up emulsions is by means of the so-called "topping plant." The general method is to pass the oil through pipe stills in which it is heated to 350° to 500° F. From the pipe still the oil passes into settling towers in which the heavy portions of the oil drop out, while the more volatile portions pass over. After passing through condensers, the water can easily be separated from the light oils.

This method is used to a considerable extent in California and is particularly adapted to the treatment of heavy oils.

CONCLUSIONS

The cost of construction and operation of these various types of installations will depend on the type of oil to be handled, the nature of the emulsion, the size of the plant, the cost of the fuel oil or electrical energy, labor conditions, and other local influences. The most suitable type of process and plant to apply to any particular locality can be determined only by studying all the conditions right on the ground. This should not be left to any concern exploiting any particular process, but to a properly qualified expert who can select the process that will operate most successfully and economically under the conditions prevailing.

Recovering Petroleum from Emulsions by Chemical Treatment

By Ralph R. Matthews and Philip A. Crosby

Roxana Petroleum Corporation, Wood River, Illinois

One of the most serious problems that producers of petroleum have encountered, from the time the first well was drilled, has been the emulsion of petroleum and water. This probably did not cause much trouble before the development of fields outside of Pennsylvania, because the petroleum produced there was of low specific gravity and water readily separated from the oil. The discovery of the asphalt base petroleum in California, and that in the mid-continent field with the so-called mixed base, furnished oils which emulsified easily and produced emulsions which were exceedingly hard to break.

The oil man has various names for petroleum emulsions, such as B. S., roily oil, cut oil, and tank bottoms, but all refer to a mixture of water (generally a brine), oil, and finely divided silt or sediment. Tank bottoms generally contain quite a proportion of crude wax or petrolatum which apparently separates from the petroleum stored in the tanks.

The oil content of such emulsions varies considerably, but will run from 10 per cent up to 98 per cent. The latter figure is given because pipe lines will accept oil with not over 2 per cent B. S. & W., and while this is not considered emulsified oil it is often exceedingly difficult to reduce much below 2 per cent.

In early days the oil producer found the easiest way to get rid of such oil was to burn it, and each had his sump in which he collected and burned emulsions. As oil became of more value, attention was turned to methods of recovering it. Various methods of heating and settling were evolved, the electrical treatment was brought forward, various chemicals were also used, and the latest development is the application of the centrifuge.

In 1917 the World War had increased the value of oil to such an extent that a serious effort was made in the mid-continent oil fields to recover emulsified oil. At that time the writers had considerable experience with a so-called chemical treatment for recovery of oil from emulsions.

RESULTS WITH SOLID COMPOUND

This chemical was known as "Tret-O-Lite" and the composition was approximately as follows:

	Per cent
Sodium oleate	83.0
Sodium resinate	5.5
Sodium silicate	5.0
Phenol	4.0
Paraffin	1.5
Water	1.0
TOTAL	100.0

It was colored blue by a very small amount of ultramarine blue which was added as an indicator during manufacture.

An aqueous solution of this compound (later work has shown a 1 per cent solution is best) was added to the emulsion in the proportion of 0.1 to 1 per cent by weight, and an intimate mixture was obtained by agitation with air or natural gas. This was allowed to stand until the emulsion "broke." To hasten this, the mixture was generally heated to about 150° F., depending on the character of the emulsion. The equipment usually consisted of wooden tanks of the desired capacity and a portable steam boiler. Thus the equipment could be moved readily from place to place.

The patentee claimed that the compound acted as a water softening agent and allowed the silt and sediment to precipitate along with the insoluble soaps formed. The oil-soluble portion of the compound decreased the surface tension of the oil films and allowed the tiny drops of water to collect and finally to separate from the oil. Analyses which the writers have made of brines from the mid-continent field lead to the belief that the above theory is probably correct, since they are uniformly of very low alkalinity and in some cases slightly acid, the result probably of hydrolysis of magnesium chloride. In fact, oil emulsions have often been "broken" by merely adding sodium carbonate and agitating thoroughly.

The B. S. & W. results in the accompanying table are typical of what was done by using the compound with tank bottoms.

	Before Treating Per cent	After Treating Per cent	Amount of Chemical Per cent by Wt.	Temp. ° F.	Time of Settling Hrs.
	20	1.0	0.7	130	26
	8	1.0	0.7	130	48
	4	0.5	0.5	130	20
	5	0.5	0.5	130	12
	8	1.0	0.6	130	24
	14	0.5	0.7	142	72
	8	0.9	0.6	142	28
	8	0.9	0.8	142	27
Av.	9	0.8	0.6	134	32

These figures show that the compound does break the emulsions readily and results in an oil recovery. The oil recovered from tank bottoms is generally not of much value for refining because of the absence of lighter hydrocarbons, and the wax content usually makes it of too high a flowing point to use as fuel oil in even moderately cold weather. The best method of handling it was found to be as a mixture with a considerable quantity of petroleum which was pumped to the refinery and handled in the usual manner.

Because petroleum is more easily refined with a minimum water content, experiments were also conducted with a view of reducing the B. S. & W., as determined by centrifuge, to below 0.1 per cent. This was done by pumping the oil from one closed tank to another, heating to not over 110° F., and adding the required chemical by a small proportional pump as the oil was moved. The oil was sampled each day, but after standing for 17 days the B. S. & W. content had dropped only from 1.5 to 0.8 per cent, and the oil showed about 0.8 per cent loss of gasoline during the settling period. Some other tests were made, but it was eventually decided that the introduction of the aqueous solution might even have a tendency to increase the B. S. & W. content of petroleum which already had a low percentage. Prolonged settling probably would not bring the amount much below 0.5 per cent, and as shown above, would result in a loss of gasoline.

LIQUID COMPOUND

After considerable experimental work, the manufacturers of this compound have developed a liquid compound. This is an aqueous solution containing about 25 per cent of sulfonated oleic acid. In its manufacture the excess acids are neutralized with caustic soda. This gives a more convenient compound to handle in the field and one which is more efficient in breaking the surface tension of the oil films surrounding the tiny drops of water; otherwise its action appears to be the same as noted above.

In the field the compound was diluted to a 1 per cent solution with a soft water, and was then fed into the oil as it was pumped. In order to get a thorough mixing of the emulsion and solution it was found necessary to put it through at least 1500 ft. of 2-in. pipe. From the 2-in. pipe the mixture discharged into a 250-bbl. wooden tank. The tank contained about 6 ft. of water, through which the discharge bubbled, removing any free water and allowing the separation to take place so that pipe line oil could be drawn off from the top. A steam coil was placed in the tank so the water could be heated if necessary.

This compound has been used very effectively in the El Dorado, Arkansas, oil field where a large amount of emulsified oil has been produced. As a typical example the following may be cited: An emulsion which could not be broken by whirling in a centrifuge was treated as outlined above with 0.03 per cent by weight at a temperature of 100° to 120° F. The yield was 75 per cent of oil with a B. S. & W. content below 2 per cent, and 25 per cent water. Working in the West Columbia, Texas, field an oil which showed 75 per cent B. S. and 25 per cent water (by centrifuge) was treated at approximately 90° F. with 0.02 per cent by weight. The yield was 60 per cent of pipe line oil and 40 per cent water.

Advantages of an Oil-Soluble Compound

The emulsions encountered in the various oil fields have in each case been found to be individual problems. The fact that it has been necessary to vary the treatment so often has led to research seeking to develop a universal compound which would break any emulsion. At the present time field experiments are being made with an oil-soluble compound with indications that it will be satisfactory. Such a compound would have the following advantages over the liquid water-soluble compound:

1—A smaller quantity would be necessary.
2—It could probably be used without heat.
3—Would not require dilution with water.
4—Would mix with oil readily.
5—Would be more convenient to handle.
6—Could probably be more universally applied.

Acknowledgment

Acknowledgment is made to Messrs. W. S. Barnickel and H. L. Barthels of W. S. Barnickel and Company for valuable assistance in the preparation of this paper.

DISCUSSION ON ELECTRICAL DEHYDRATION OF CRUDE OIL

By W. G. and H. C. Eddy

927 Higgins Building, Los Angeles, California

A more appropriate title of this discussion would be, "The Electrical Process of De-emulsification." A new era dawned on the oil industry when Dr. Cottrell proved that emulsion is essentially oil and water—an intimate mixture to be sure but nevertheless nothing but a mechanical mixture that can be broken down electrically and separated into pipe line oil and oil-free water.

When an emulsion is subjected to the influence of a high potential alternating field the minute water particles, electrically charged by the field, rupture the enveloping oil films and coalesce, forming larger water droplets. This action of stress and strain, attraction and repulsion, on the conducting water particles continues until all the microscopic drops of water in the original emulsion have broken the bonds of the entrapping oil films, the larger droplets serving as nuclei until the entire water content is freed into large drops which readily settle out. The action of the electric current is easily followed in the micro moving picture film, and under the microscope the breaking up of the emulsion is accomplished in a few seconds.

The low power requirements of the process, from the records of commercial plants, substantiate the theory that the phenomenon is that of a multitude of series condensers rather than of conducting paths. The minute water particles serve as the electrodes or poles of the condensers and the separating oil acts as the dielectric which is ruptured by the high voltage, allowing adjacent positively and negatively charged droplets to neutralize themselves by uniting.

The Electric Dehydrator

The dehydrator consists of the electrical treater and a settling trap. The treater is a galvanized steel tank approximately 3 ft. in diameter and 8 ft. high; in the center of this is suspended a vertical shaft which carries a number of circular disks. This shaft is supported by an insulated bearing and rotated at a slow speed by a small electric motor. A potential of approximately 11,000 volts alternating current of any commercial frequency is impressed between the revolving electrode and the tank shell which constitutes the other electrode, and is grounded. The usual supply circuit is one of 220 voltage and the current passes through a suitable switchboard and regulating coil and is stepped up by a transformer to the required high potential.

The emulsified oil is fed continuously to the treater, passing into and through the annular electric fields formed between the edges of the disks and the treater shell, where the de-emulsification takes place. The freed oil and water pass into the trap tank where they separate, the oil flowing from the top to the shipping tanks, while from the bottom flows the liberated water, together with the salts in solution.

A plant utilizing a single transformer, motor and trap may consist of any number of treaters from one to eight in even multiples. The capacity averages from 300 to 1000 bbls. per day per treater depending on the character of the emulsion, some treaters having demonstrated a capacity over 1600 bbls.

The electric power consumption ranges from 5 to 75 watt hours per bbl. of cleaned oil, the cost of electricity averaging one cent for 20 to 50 bbls.

The fundamental process on which Dr. Cottrell obtained basic patents is known as the Cottrell process for separating one liquid suspended in another. There are many ways of putting this principle into practice with various shapes and sizes of electrodes and containers, and much experimental work has been done in determining the most effective frequency, voltage, and size of field applicable to various emulsions.

One outstanding feature of the electric process is its lack of limitation. "All is grist that comes to the electric mill;" it is handling all types of emulsions, of all percentages, viscosities, and gravities. In fact, the ease of de-emulsification often increases with an increased water content up to 30 or 40 per cent, while larger percentages reduce slightly the gross daily capacity per treater. Re-treatment in field practice has never been found necessary, even on tank bottoms testing 95 per cent emulsion, which are treated successfully, reducing the water content to a fraction of 1 per cent. In California and the Gulf Coast fields it has become the standard method of dehydration. Ninety-five per cent of the emulsion treated in California is handled by the electric process. Even where the crude oil is topped an electric dehydrator is often installed ahead of the topping plant.

A record of eight years of field operation established the upkeep expense as not over $15 per treater per year. The total cost, including steam, electricity, royalty, labor, repairs, interest and depreciation, has been found to be from one to three cents per barrel of net oil.

While a number of these electric plants are operated at atmospheric temperatures, there is usually a certain critical temperature, varying somewhat with different emulsions, at which the plant shows its maximum capacity. The highest temperature used on extremely rebellious and viscous emulsions is 180° F. and the average temperature of all plants operating is 135° F. The lower gravity oils usually require a certain amount of heat before they can be handled or pumped satisfactorily. At this temperature the emulsion ordinarily can be broken up electrically, thereby saving not only a large amount of fuel but also the volatiles, which would be lost at higher temperatures. In handling high gravity oils an enclosed-type treater operating under pressure retains in the oil practically all the lighter constituents.

A typical California installation in the Coalinga field consists of eight units on one transformer circuit and has a capacity of 8000 bbls. daily, working on a 15 to 20 per cent emulsion, the gravity of which is 16° Bé., and operating at 140° F. The heat is supplied by utilizing the exhaust from the compressor plant. The compressor plant attendant also operates the dehydrator.

NOTE: The paper by Dr. Leon W. Parsons on "The Inversion of Phases in Oil-Water Emulsions," which was the opening paper of this symposium, will be published in the December issue of THIS JOURNAL.

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

The Removal of Free Acid from Nitrocellulose with Special Reference to the Use of Saline Leaches[1,2]

By S. E. Sheppard

RESEARCH LABORATORY, EASTMAN KODAK CO., ROCHESTER, NEW YORK

Whether nitrocellulose is to be used for lacquers, for celluloid, for photographic film support, or for explosives, the removal of excess acid leaving a neutral material is essential. Without dilating on the history of the matter[3] it may be noted that it was early recognized that thorough purification of nitrocellulose from excess acids is essential to obtaining a stable product. We may, however, note that while removal of free acid is a necessary, it is not, alone, a sufficient condition for stability. The uncertainty as to the part played by residual "free" acid in affecting stability has been largely due to the absence of any method for determining the "free" acid occluded in the fibrous mass. We shall revert to this point later, when noting a method developed in this laboratory which makes this possible.

It was found early in the history of the industry that washing with cold water alone effected the removal of acid very slowly and imperfectly, and that stable products were not obtained. This procedure was supplemented, therefore, by the use of dilute alkalies to neutralize any free acid. Great caution was necessary in this, since excess alkali rapidly hydrolyzes the higher nitrates of cellulose.

The introduction by Sir F. Abel[4] of the method of pulping was based on the idea that instability was due to free acids remaining in the tube of the cotton fiber, and that by mechanically cutting these tubes acid was more readily and completely removed. Actually it is improbable that such an action takes place. The "capillarity" of cellulose, and of nitrocellulose, particularly nitrocotton, has nothing to do with the tube of the individual cell, but with the interstices of the felted masses of fibers, *i. e.*, it is not intrafibrillar but interfibrillar.[5]

The quite real advantage of pulping, especially in conjunction with the later "boiling" process of stabilization, consists in affording an early opportunity for blending and homogenizing the very variable and inhomogeneous product, nitrocellulose,[6] and in insuring that the washing and stabilizing treatment is not held up in clumps and knots of the fiber. It is indeed possible that undesirable substances, other than acids, are removed from the tubes in this way, but it is not easy to demonstrate this on a small scale. We have found in the course of this investigation that it is quite as easy to stabilize small quantities—up to 1 lb.—of nitrocotton, long or short fiber, by boiling processes without any pulping as when pulped. We consider, therefore, that the main value of pulping consists in the hydraulic handling of large masses, as already noted.

The combined process of pulping and boiling,[1] representing both high initial outlay and high running charges, has been chiefly confined to the manufacture of guncotton, etc., less drastic methods being used in the celluloid and allied industries. In these pulping is often used, as facilitating handling, but not the stabilizing treatment by boiling.[2]

The view has been frequently expressed that removal of "free" acid, to the last traces, is in itself insufficient to secure high stability, and that conversely the presence of "free" acid is not in itself sufficient cause of instability, at any rate immediately. Evidence was obtained in the course of this work supporting these conclusions. It appears, therefore, desirable that the washing out of "free" acid should be differentiated from stabilization, and as problems, investigated each for itself, although with due regard to a considerable measure of contingency of the two problems.

With this we will detail certain conclusions reached in this laboratory as a result of work extending over several years.

WASHING OUT ACID AND ADSORPTION

It is well known that the washing out of a soluble component from an otherwise insoluble material is, in the absence of selective adsorption, representable by an equation giving the quantity of extractable material remaining after successive washings with the same volume of fresh solvent, as follows:[3]

$$X_n = \left(\frac{v}{V + v}\right)^n X_o$$

where X_o = total quantity of extractable substance.
X_n = quantity remaining after n extraction.
v = volume of liquid remaining on precipitate or material.
V = volume of solvent used in each extraction.

We may note the following important practical conditions expressed by this equation:

1—The amount left unextracted will be smaller, the less the fraction $v/(V + v)$; this will be smaller, the better the drainage

---

[1] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Communication No. 115 from the Research Laboratory of the Eastman Kodak Company.

[3] A. Marshall, "Explosives," Blakiston, **1915**, 161.

[4] Brit. Patent 1102 (1865).

[5] A. de Mosenthal, *J. Soc. Chem. Ind.*, **23** (1904), 292.

[6] Robertson, *Ibid.*, **25** (1906), 624

[1] Marshall, *Loc. cit.*

[2] See Bonwitt, "Das Zelluloid," **1912**.

[3] See W. Ostwald, "Foundation of Analytical Chemistry," 2nd Eng. Ed., p. 15.

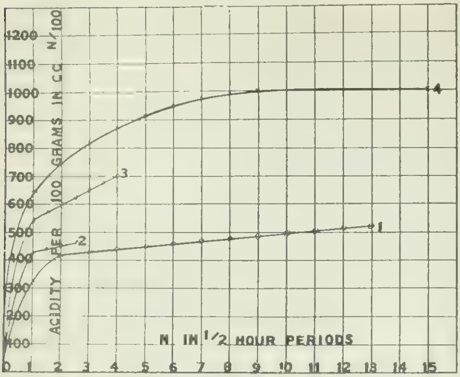


Fig. 1

1—Distilled Water at Rest Natural Drainage; 2—Distilled Water Agitated, Natural Drainage; 3—Distilled Water Agitated, Centrifugal Drainage; 4—Bicarbonate Water

between successive washings, since this makes V large compared with v.

2—The equation assumes that the period of each washing (or extraction) is long enough for a state of equilibrium to be reached between the extractable substance in the solid material and that in the wash water. Continuous washing is relatively uneconomical in regard to volume of liquid required, one reason being that equilibrium is not always satisfactorily reached under this condition.

3—The equation further assumes that X_o, the total quantity extractable, is definite, and that there is no selective absorption of the extractable substance to the precipitate or other material.

Evidently if the solid material itself undergoes a reaction, such as hydrolysis, with the solvent, furnishing thereby the same or a similar substance to that being extracted, the value of X becomes less definitive, in proportion to the magnitude of the hydrolysis. Now the nitrates of cellulose are susceptible of hydrolysis, the rate being a pronounced function of the concentration of hydroxyl and hydrogen ions.[1] It can be shown, however, that for values near neutrality and at not too high temperatures, the rate of hydrolysis is small compared with the rate of extraction of free acid.

It is evident that such hydrolysis would tend to increase both X and X_o. Actually, however, as will now be shown, the rate of removal of "free" acid from nitrocellulose, and in particular nitrocotton, falls much below that indicated by the formula.

For reasons which will be subsequently detailed, we regard this as due to selective adsorption of acid to the nitrocellulose. It is possible that the cellulose nitrates are themselves derivatives of, or their formation involves the production of, hydrocellulose. Whether the adsorption of acid is due to residual unnitrated cellulose, to disintegrated cellulosic residues of the so-called cellulose dextrin type, or definitively to the nitrated part of the complex, cannot be stated conclusively at present.

Experimental Procedure

In the earliest stages of this work the determination of the total "free" acid present—the retained acid—initially, corresponding to the value X_o in the extraction equation, was taken as the final value obtainable by prolonged extraction with very dilute bicarbonate solution, or by the leaching process subsequently detailed. It is evidently unadvisable to use more drastic treatments involving hydrolysis. This determination was greatly facilitated and its reliability improved by a method worked out during the course of the investigation by Messrs. L. Schneider and W. H. Davis. This method consists in dissolving the nitrocellulose in acetone[1] and adding just sufficient water, with thorough stirring, to precipitate the nitrocellulose as a fine stable suspension—in fact, largely colloidal in character. It is then possible to titrate the retained acid directly, using methyl red as indicator. In operation, usually 2 g. of nitrocellulose are dissolved in 50 cc. of acetone, and 50 cc. of distilled water are added with thorough stirring. The acid present in the turbid liquor is titrated with 0.01 N potassium hydroxide, using 3 drops of methyl red indicator, 2 g. per 100 cc. alcohol. The precipitation and titration are best carried out in square, wide-mouthed bottles of about 4-oz. capacity. The acetone used is titrated for the "blank" and a correction applied when necessary. By this means the X_o of the extraction formula can be found directly. The values so obtained agreed very well with those found by the exhaustive extraction processes referred to, but the direct method is in many respects more satisfactory, as well as time-saving. For actual determination of X_o in the course of the extraction experiments the procedure adopted was a combination one, the acid removed being determined as outside (extracted) acid, and the final residual acid in the *sample under treatment* being determined by the method just described. The sum of these is then taken as X_o, the total quantity of retained acid.

The nitrocellulose used in these experiments was specially prepared. The nitrogen content was varied from 9 to 13 per cent, and nitrocellulose from both cotton and purified sulfite pulp cellulose was tested.

Action of Distilled Water, Compared with That of Hard Water, and at Different Temperatures

In the small, laboratory-scale experiments, charges of 100 to 200 g. (moist weight) of nitrocotton were placed in colanders and left for a period, usually 1 hr., in porcelain beakers containing the water. Drainage was effected either by:

1—Natural drainage.
2—Centrifugal drainage.
3—Squeeze roll drainage, using an ordinary laundry wringer.

In certain cases, as mentioned later, the material was not left at rest, but agitated, either by blowing air under pressure (air-beating) or by a mechanical agitator. The removal of acid was followed by titrating the drained-off wash liquid, of measured volume, with 0.1 N and 0.01 N alkali (NaOH solution), using methyl red as indicator.

This indicator has a range of pH 4.2–6.6. In the titrations the mean was taken of forward and back titrations, corresponding to a pH = 6.0. To economize space the data are given as far as possible graphically, tables not being given except where specifically desirable.

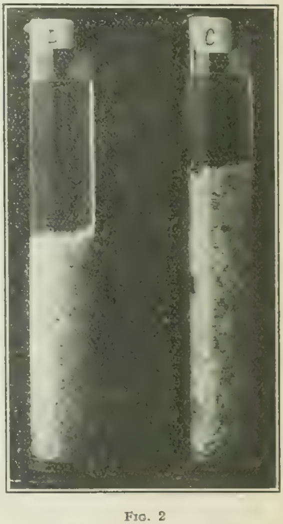


Fig. 2
L—Short Fiber, C—Long Fiber

---

[1] Robertson, *Loc. cit*

[1] Nitrocelluloses insoluble in acetone, but soluble in ether-alcohol, can be used by adding first an equal volume of acetone to the ether-alcohol solution.

In the graphical exposition, Fig. 1, the "acidity" removed, plotted as ordinate against "extraction periods," is expressed reciprocally in cc. of 0.01 *N* alkali neutralized. The ratio of nitric to sulfuric acid in the acid removed was not generally determined, although in view of the theoretical interest estimations were made in certain cases, as also of nitrous acid. The curves in Fig. 1, which are typical of a great number measured in the course of the work, bring out the following facts: With distilled water (Curve 1), the extractions, after proceeding initially at a rapid rate, soon reach a stage during which the removal is extremely slow. The rate of removal in this period, for distilled water, is slightly increased by agitation (Curve 2), and considerably by centrifugal drainage at each change (Curve 3). Even so, it remains much below the rate in the presence of dilute alkali (calcium bicarbonate of hard water) (Curve 4). Further, it does not follow the extraction function already discussed, the actual rate being very much less than this would indicate. This function,

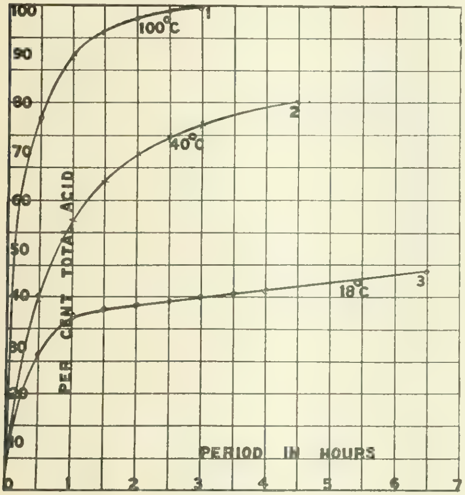


Fig. 3

$$X_n = \left(\frac{v}{v + V}\right)_n X_o,$$

for constant values of *v* and V—these being fixed for constant experimental conditions—can be written

$$\frac{X_o}{X_n} = a^{-n} = b^n, \text{ where } b = \frac{1}{a},$$

or, taking logarithms,

$$\log \frac{X_o}{X_n} = n \log b = nA,$$

whence, differentiating,

$$\frac{dx}{dn} = K\ (X_n),$$

i. e., the rate of removal is proportional to the quantity left unextracted. With distilled water, at room temperature, however, the rate of removal appears to be affected by an impeding or opposing effect, which is a function of the external acidity and of the condition of the fibers; *i. e.*, we have

$$\frac{dx}{dn} = K\ X_n - f\ (X).$$

This opposing influence is overcome by increase of temperature or alkali; we consider that it is due to selective adsorption of the acid. This view is supported by the action of concentrated neutral saline leaches, to be discussed immediately. The formation of cellulose esters, involving the elimination of water from the cellulose complex, is in principle a reversible reaction, in which esterification is opposed by hydrolysis.[1]

In the case of nitrocellulose the reverse reaction of saponification or hydrolysis is usually accompanied or followed by breakdown of the cellulose complex,[2] and such degradation products are formed in nitration and esterification. It is possible that for any cellulose ester in contact with water there is a mobile equilibrium between acid in three different strata or stages:

1—Acid in mechanically adherent and external liquid.
2—Acid in adsorption layer.
3—Acid residues of cellulose ester

While equilibrium between 1 and 2 is rapidly adjusted that between 2 and 3 is more slowly effected, corresponding to the breakdown rate (hydrolysis) of the esters of cellulose and its degradation products.

The Effect of Mechanical Drainage

The effect of mechanical drainage, illustrated in Fig. 1, is entirely in accord with the extraction function, as lessening the volume *v* of adherent liquid. The advantage of mechanical drainage is, however, not only due to this; in addition, the fibrous mass becomes compressed by such means, and on re-immersion in the liquid soaks this up like a sponge, thus insuring rapid and more complete contact with the liquid, for which purpose it is largely equivalent to agitation during extraction, depending upon the fiber length of the cellulose. In Fig. 2 is shown a comparison of the relative "active bulks" in water of two samples of "long" and "short" fiber cotton, respectively. The capillary effect of a mass of long fiber cotton in washing or leaching without agitation is considerably greater than for short fiber material, the elasticity of the long fibers tending to keep the mass looser and more permeable. It mats to relatively easily penetrated felts with long capillary interspaces, while with shorter fibers a denser "balling up" is possible.

Temperature Coefficient of Extraction

The temperature coefficient of extraction of acid by distilled water is very high. This is shown in the curves in Fig. 3.

It is much greater than would follow from simple increase in the rate of diffusion of acid, and this points to a disturbance of the adsorption equilibrium. As the temperature approaches the boiling point, there is liable to occur some release of extra acid above that extracted by treatment at lower temperatures, and indeed above that shown as "retained free acid" by the direct analytical method described. This acid must be released from ester-like combination, probably with lower cellulosic residues (degradation products of cellulose).

The amount, however, due to this was seldom found to be at all considerable in properly nitrated cellulose, and did not appear to bear much relation to instability. This point is referred to later, in dealing with the relation of stabilizing processes to acid removal.

Acid Removal by Leaching with Concentrated Neutral Salt Solutions

At the time these investigations were commenced we were checking up experimentally H. R. Procter's[3] work on the swelling of gelatin in acids, using his method of removing imbibed acid by treatment with sodium sulfate. Since cellulose gives evidence of behaving as an amphoteric colloid it appeared

---

[1] E. Berle and Klaye, *Z. Schiess. Sprengstoff.*, **2** (1901), 425; *J. Soc. Chem. Ind.*, **27** (1908), 534.

[2] Denitration with sodium sulfide is possible.

[3] H. R. Procter, *J. Chem. Soc.*, **105** (1914), 313.

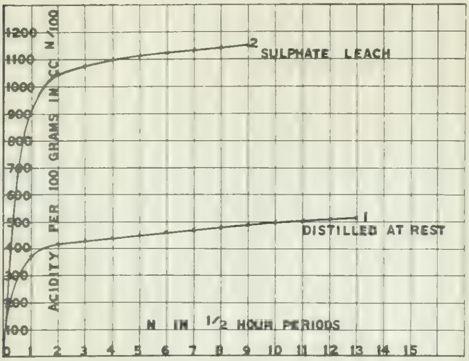


Fig. 4

worth trying whether a concentrated neutral salt solution would facilitate the removal of acid from nitrocellulose. This was found to be the case.[1] A neutral solution of sodium sulfate was found to displace "free" acid from nitrocotton very rapidly. The curves in Fig. 4 illustrate this.

It will be seen that the action is much more efficient, at room temperature (18° to 20°) than either distilled water or hard water of moderate bicarbonate alkalinity. The "hard water" used had a total alkalinity of 16 cc. 0.01 N alkali per 100 cc.

The concentration of solution found most satisfactory is one somewhat below saturation at 18° to 20° C., having a specific gravity of 1.140. The data on the equilibrium of Na_2SO_4 and water at different temperatures were plotted as a graph, and the relation of the specific gravity of sodium sulfate solutions to the composition or concentration. The graph is useful for the purpose of preparing and regenerating such baths on a large scale. After the first laboratory experiments with 100- and 200-g. lots, trials were made on a larger scale. These larger scale experiments fully confirmed the deacidifying action of sodium sulfate leaches.

WASHING OUT SODIUM SULFATE—It was early found on a laboratory scale that the excess sodium sulfate was washed out by water very readily, and practically in accordance with the extraction formula. The neutral salt, unlike acid, is not adsorbed to the nitrocellulose.

THEORY OF THE ACTION OF NEUTRAL SALT LEACH

Before proceeding with an account of the practical application of the sulfate leach in the treatment of nitrocellulose, it will be well to consider the theory of its action. As it is hoped to take up the theoretical aspect more fully on another occasion it will only be briefly noticed here. The discovery of the deacidifying action of a strong neutral salt leach was due originally to an application of Procter and Wilson's work on gelatin.[2] According to their theory, when gelatin is immersed in a dilute acid, combination takes place between the gelatin molecules and the hydrogen ions, resulting in the formation of a highly ionizable salt of gelatin; the salt is hydrolyzable, and swelling, or hydration, is regarded as due to the ionization of the salt and the osmotic pressure so produced. The resultant equilibrium was worked out in terms of Donnan's theory[3] of membrane equilibrium and good agreement between observed and calculated values obtained. Addition of neutral salt solution to a gelatin swollen in acid depresses the ionization of the gelatin salt, and dehydrates the jelly and displaces acid from combination with the colloid. It is not proposed to enter into the quantitative aspect of the theory here, although this is its strongest feature. It is, however, evident that if this theory applies to the present case we must assume that the adsorption of acid to nitrocellulose depends upon the formation of a salt-like, ionizable (non-ester) combination between the cellulose complex and acids. It is very possible that it is not so much cellulose itself or the cellulose ester which is active here, as degradation products of the cellulose, *e.g.*, cellulose dextrins. Qualitatively in agreement with the Procter theory is the fact that other saline leaches were found effective, as magnesium sulfate, sodium acetate, and sodium chloride. The last named was not as efficient as sodium sulfate. Further evidence for the general thesis of selective adsorption of acid and of ionic displacement, concomitant with dehydration, will be brought forward in dealing with pulping. In considering the application of Procter's theory to the present case of cellulose esters, it is to be remarked that the actual hydration (or swelling) and adsorption here is very small compared with gelatin. Further, it may be remarked that the general thesis does not stand or fall with Procter's conception. The adsorption of acid may not be due to definite chemical combination but to electrostatic forces,[1] and the action, *e. g.*, of sulfates, due to removal of adsorbed hydrogen ion by the reaction

$$\overset{+}{H} + \overset{--}{SO_4} \rightleftharpoons \overset{-}{HSO_4}.$$

In any case, the action of the sodium sulfate leach is to make the removal of acid fall in line with the extraction formula previously considered, differing from the case of distilled water. This is illustrated by the following case of the extraction of acid from two portions of the same sample of dipped and wrung nitrocotton, one treated with distilled water, the other with sodium sulfate leach. The total retained acid, determined as described, was equivalent to 1150 cc. 0.01 N acid per 100 g. nitrocotton. In Table I are given the total acid extracted after n changes (the volume being made up to the same value after each drainage) and the acid left unextracted.

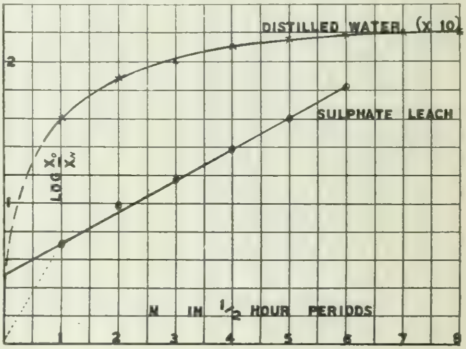


Fig. 5

Calling X_o the total extractable acid, and X_n the amount remaining retained after n extractions, it follows from the simple extraction function that log X_o/X_n should be a linear function of n. In Fig. 5 the values of log X_o/X_n have been plotted as ordinates against n as abscissae, the scale for the distilled water values of log X_o/X_n being ten times that for

---

[1] S. E. Sheppard, U. S. Patent 1,357,733 (November 2, 1920), assigned to Eastman Kodak Company.

[2] H. R. Procter, *Loc. cit.*; H. R. Procter and J. A. Wilson, *J. Chem. Soc.*, **109** (1916), 307.

[3] F. G. Donnan, *Z. Elektrochem.* **17** (1911), 572, also W. McLewis, "System," II, 309.

[1] W. D. Bancroft, "Applied Colloid Chemistry," **1921**.

TABLE I

No. of Leaches	—Acid Extracted—		—Acid Remaining—	
	Dist. H_2O	Sulfate	Dist. H_2O	Sulfate
n	Cc.	Cc.	Cc.	Cc.
1	364	925	786	225
2	412	1045	738	105
3	430	1075	720	75
4	444	1100	706	50
5	454	1120	696	30
6	461	1135	689	15
7	467	..	683	..
8	472	..	678	..

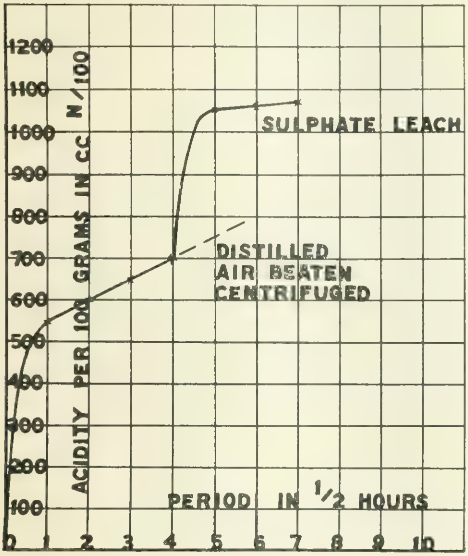


FIG 6

sulfate, owing to their low value. It will be seen that in the case of the sulfate leach a straight line is obtained, while for distilled water this is not the case. For absolute agreement with the theory, the line should go through the origin $n = 0$, whereas actually it cuts the abscissae for a negative value of n, which indicates that extraction proceeds more rapidly in the first leach than in the subsequent steady state.

The great difference between the action of the sulfate leach and of distilled water is strikingly shown in Fig. 6. The first part of the curve shows the progress of acid extraction from a nitrocotton by distilled water which was both agitated during leaching and centrifugally drained between washings. After four such treatments water was replaced by sulfate leach with the result shown in the curve.

REGENERATION OF SULFATE LEACH

Returning to the practical aspect of sulfate leaching, it has been noted that the acids removed during leaching may be neutralized and the same leach used over again. In laboratory and small-scale experiments this resetting of the leach was at first effected by determining the total acidity by titration of an aliquot part, and adding the requisite amount of sodium carbonate to secure neutrality. On a large scale such a procedure is neither convenient nor reliable. Methods of automatic regeneration were therefore developed. The first method consists in collecting the leach liquors as they come from the final leaching tank or vessel, in a large regenerating tank, provided with heating coils for winter temperatures, with a mechanical agitator, and also piped for compressed air agitation.

The acid leach is neutralized in this by the introduction of definite charges of finely divided calcium carbonate. Either finely pulverized marble or high calcium limestone may be used, the $CaCO_3$ content being of the order 95 per cent +. Limestones containing magnesium are not generally suitable. The material should be so pulverized that 85 per cent passes 200 mesh, and 95 per cent passes 100 mesh; under these conditions over 95 per cent of the material is active in neutralization of sulfuric acid. As the solution becomes charged with carbonic acid it is liable to dissolve excessive amounts of lime salts in the form of calcium bicarbonate. To prevent this, the mixture in the tank is thoroughly aerated with compressed air, thus discharging carbon dioxide and keeping the lime content down. At the same time this aeration, in the faintly alkaline solution, removes iron extracted from the nitrocotton by the first acid leaches; the iron is thrown out as hydrous ferric oxide, adsorbed and held by the sludge.

This retention of iron improves as the sludge accumulates and becomes impregnated with the hydrous oxide, as it then functions similarly to the well-known method of Spring for clearing such colloidal hydrous oxides from solution. Coagulation is assisted by the high electrolyte content (Na_2SO_4) and is further improved by heating. A certain amount of coloring matter is removed at the same time. As the operation is repeated, from time to time excess sludge is removed, sufficient being left to exert the helpful action in removing iron and coloring matters. The neutralized leach, clarified as far as convenient by sedimentation in the regeneration tank, is then filtered.

Where bleaching of the nitrocellulose is desirable, as in celluloid manufacture, the sulfate leaching process can be readily combined with the bleaching process.

RELATION OF SALINE LEACHING TO STABILITY AND CONJUNCTION WITH BOILING PROCESSES

The sulfate leaching process at ordinary temperatures does not produce highly stable nitrocellulose. The product of a normal nitration when thus treated is, however, already of considerably higher stability than the same nitrocotton deacidified by repeated washings with weakly alkaline water at ordinary temperatures. Table II illustrates this, the stability test used being the 135° C. heat test[1] which has been found[2] to give results very sensibly parallel with Wills' stability test, based on the rate of decomposition in a stream of carbon dioxide at 100° C.

TABLE II —IMPROVEMENT IN STABILITY OF NITROCOTTON LEACHED WITH Na_2SO_4 AQ., 135° C. STABILITY TEST

No.	Treatment	Litmus Time Min.	Fume Time Min.	Explosion Time
1	Hard water 10 changes in 6 days	5	5	18 min.
2	Hard water 16 changes in 267 hrs.	25	35	Not 5 hrs.
3	9 changes in 140 hrs.	5	5	20 min.
4	20 changes in 10 days	10–15	10–15	5 explosions out of 10
		(Average of 10 experiments)		
5	Sulfate leach 8 changes in 8 hrs.	20	25	Not 5 hrs.
b	with one	20	45	Not 5 hrs.
c	with two alkaline washes	42	240	Not 5 hrs.

In the experiments just recorded, the excess sulfate had been washed out of the nitrocellulose to a point lower than the solubility of calcium sulfate. It is actually quite feasible to leave more sodium sulfate in the nitrocellulose than this. Our experiments show that up to 3 per cent sodium sulfate, based on dry weight of nitrocellulose, may be left without causing turbidity in a 20 per cent solution in acetone[1] and without affecting the physical properties of celluloid made from the nitrocotton.[2] It was of interest to determine the effect of residual sodium sulfate on the heat stability of nitrocotton. The set of experiments in Table III are typical. They show that up to a certain amount the heat test at 135° C. is raised, and after this it goes down again.

---

[1] Marshall, *Loc. cit.*

[2] By Mr. H. LeB. Gray and assistants of the Organic Chemistry Department of the Research Laboratory of the Eastman Kodak Co., in an investigation as yet unpublished.

TABLE III—HEAT TEST AND SODIUM SULFATE CONTENT

Na_2SO_4 in Bath Per cent	Litmus Min.	Fume Min.	Explosion
0	10–15	10–15	Not 4 hrs.
0.005	10–15	10–15	Not 4 hrs.
1.0	26	32	Not 4 hrs
2.0	50	60	Not 4 hrs.
4.0	22	26	Not 4 hrs.
6.0	23	25	Not 4 hrs.
8.0	18	18	Not 4 hrs.

Although the sulfate leach improves the stability over that by cold alkaline washes, and leaving small amounts of sulfate in the cotton appears beneficial, the result is not satisfactory where the highest stability is necessary. To obtain this there is no doubt that hydrolysis at high temperatures is essential, substantially according to the boiling processes in use in various systems. In the last issue, in large-scale work, the intensity and durations of such hydrolytic treatment must be worked out in relation to the particular régime of nitration, degree of nitration, purpose of the nitrocellulose, etc.[3] It was, however, fundamentally important to ascertain if such a treatment could be readily combined with the sulfate leaching process. That is, it was necessary to determine whether equal stabilities were obtained with the same nitrated cottons hydrolyzed in water and in sodium sulfate solution, at the same acidity.

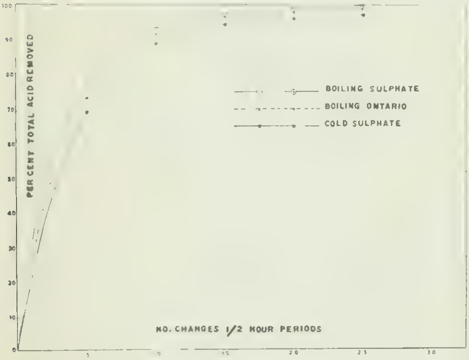


FIG. 7

Table IV gives data showing that boiling in sulfate is equally effective with boiling in water in raising the stability. In each case the same régime in boiling and washing or leaching was followed.

Further, these experiments demonstrate that, in small samples, boiling gives high stability without pulping, indicating that the value of this operation is principally in regard to the homogenizing of large masses. The curves in Fig. 7 give comparisons in the efficiency of acid removal by straight treatments with sulfate and water used at high temperatures.

TABLE IV—STABILIZATION BY BOILING, 135° C. TEST

No	Treatment	Litmus Time Min.	Fume Time Min.	Explosion Time
1	Washed hard water 20 changes, not boiled (6 days)	10	15	Not 4 hrs
2	Leached cold sulfate, 8 changes	15	25	Not 4 hrs.
3	Hard water boiled	90	180	Not 5 hrs.
4	Hard water (twice bicarbonate of No. 3)	120	None observed	
5	Sulfate leach boiled. Water as in No. 3	90	180 to 240	Not 5 hrs
6	Sulfate leach boiled. Water as in No. 4	150	None observed	Not 5 hrs.

FURTHER NOTES ON STABILIZATION

The acid boiling on hydrolysis operation is regarded as greatly dependent on acidity, being usually regarded as a hydrolytic decomposition of cellulose acid sulfate, catalytically influenced by H-ion concentration.[1] It might, therefore, be thought that the presence of concentrated sodium sulfate, tending to decrease the H-ion concentration, would reduce the efficiency. Our results do not show any evidence for this, as regards stability effected, time necessary, or amount of sulfuric acid released. Much recent work has shown that most acid catalysis is dual, the undissociated molecules being equally efficient with the H-ion.[2] We regard the theory of decomposition of cellulose sulfates and nitrates as unsatisfactory. The reaction mechanism, for example, considered by Robertson apparently assumes a reaction in aqueous solution, whereas it probably takes place in quasisolid solution, in the adsorption layer of the membrane, so that quite other concepts than mass action in aqueous solution plus H-ion catalysis are necessary.

Moreover, there is considerable doubt as to whether the cellulose sulfuric esters greatly affect true stability.[3] In our own experiments we found that for certain nitrocotton samples high stability by heat and decomposition tests was achieved early by short boiling in water or sulfate solutions of quite varied acidity. With other samples, very prolonged boiling with acid solutions failed to produce any satisfactory stability, but making the solutions faintly alkaline immediately raised it. As this paper is not primarily concerned with stabilization we will not dilate further on these points. We may note, however, an experiment which indicates the possibility of a very definite colloid chemical factor in relation to stability and instability. After preparing the colloid suspensions of nitrocellulose in 50:50 acetone and water, it was desired to ascertain if the acid was free in the liquid phase, or still adsorbed to the nitrocellulose particles. By using a Sharples laboratory high-speed centrifuge it was found possible to remove the suspended nitrocellulose. The residual liquor was titrated, with results which showed that the acid estimated by this procedure is very little adsorbed by the particles, and that only free acid is determined, not acid combined as ester. In working on this, it was further found that by using a graduated increase of water, and, better still, by using the same amount of water with different concentrations of sodium sulfate, and centrifuging, a fractionation of the nitrocellulose could be effected from the colloid suspensions. Stability tests on these fractions showed that the first fractions contained the least stable materials, later fractions having good stability. The more ready agglutination and precipitation from aqueous acetone of the unstable portions is in agreement with the view that much of the instabilizing impurities in nitrocelluloses are nitrated hydrocellulose or cellulose-dextrin bodies, derived from cellulose by hydrolytic breakdown. These are normally strongly adsorbed to the stable ester, being formed in the membrane or semplar of cellulose micelles. Loosening or peptization of these complexes can be effected by weak acetone-water solutions,[1] by hot water, and by hot aqueous solutions. The possibility of fractional coagulation and centrifugal separation from more concentrated aqueous acetone suspensions opens up a field of application of colloid chemical considerations to the stabilizing process which is of both theoretical and practical importance. The frequently asserted direct stabilizing value of the Abel beater treatment (apart from considerations of bulk homogenizing) may well depend much more upon mechanical separation of such adsorption combinations than upon release of acids, etc., inside the tubes and cells. On this view, "stabilizing" depends much less upon chemical destruction of cellulose sulfuric esters, and of lower nitrates of cellulose, than upon peptization and removal of cellulose dextrin, etc., derivatives, to which mechanical, thermal, and chemical agencies can all contribute, but may also hinder, by facilitating resorption. The colloid chemical theory of lignocellulose urged by H. Wislicenus[2] should be considered in this connection. On this view, the *purification processes for "nitrocellulose" are technologically continuous with the processes for the purification of cellulose itself, notably of cellulose from lignocellulose.* This idea is supported by the process of stabilization developed in Germany during the war by Schrimpff,[3] which consists in boiling the nitrocellulose in concentrated (up to 30 per cent) solutions of sodium bisulfite.

---

[1] Turbidity (or clarity) measured by the turbidimeter described by S. E. Sheppard, THIS JOURNAL, **12** (1920), 167.

[2] Viscosity of solution, strength of film.

[3] R. Robertson, *Loc. cit.*

[1] Stadlinger, *Kunststoffe*, **1912**, 403, *et seq.*; Robertson, *Loc. cit.*

[2] Goldschmidt, *Z. phys. Chem.*, **70** (1910), 627; **81** (1912), 30; Acree, *Am. Chem. J.*, **48** (1921), 352.

[3] A. Schrimpff, "Nitrocellulose," J. F. Lehmann, Munich, **1919**, 80.

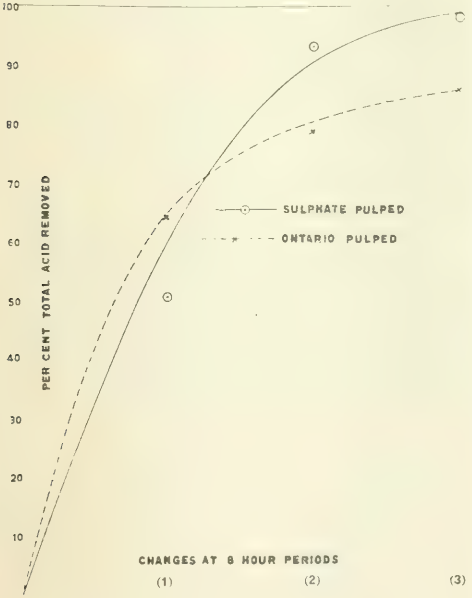


Fig. 8

In sum, it is probable that the conceptions as to instability and stabilization[4] hitherto dominant[5] have been too purely chemical, and that lack of appreciation of the colloid chemical aspect of the problem has caused and is causing much waste of time and energy in government and industrial handling of nitrocellulose.

Fig. 9

Combination of Sulfate Leaching with Pulping

A comparison of extraction of acid combined with pulping, between hard water[1] and sodium sulfate leach, respectively, is shown in Fig. 8.

In these experiments ball mills were used to wet grind and pulp the nitrocotton. Two identical mills were run off the same shaft, and equal charges of nitrocotton, flint balls and liquid (water or sulfate leach) were placed in the mills. Both long and short fibered cotton were used, but it was necessary to cut up the former before milling to secure a disintegrating action in a reasonable time. Mills were used because a small hollander was not available, but there was the advantage that the pulped nitrocellulose did not become contaminated with metal;[2] on the other hand the "beating" action of the ball mill produced a higher dispersity than would be practically desirable.

The first point of importance brought out by these experiments was that in all cases, both for long- and short-fiber cotton, it was found that the nitrocotton offered much greater resistance to pulping in the sulfate leach than it did in water. Approximately two to three times as long was required to effect the same degree of disintegration in sulfate leach as in water. This appears to be in good agreement with the theory we have advanced, that the action of sulfate in removing acid consists in an osmotic effect on the fiber membrane, tending to dehydrate this and expel both water and acid. Such an action, astringent in character, should temporarily increase the fiber strength and resistance to mechanical disintegration. These pulping tests at the same time brought out strongly the greatly superior efficiency of sulfate leach over water in removing acid at ordinary temperatures. The following data, shown graphically in part in Fig. 8, illustrate this:

"Hard" Water Pulping

Nitrocotton No. 578 soused	Short fiber
Weight of soused cotton	600 g.
Weight of moist pulp	253 g. drained
Weight of dry nitrocotton	101.2 g.

Water changed 3 times in 24 hrs.

Alkalinity of Water = 16 cc. 0.01 *N* alkali per 100 cc.

No. of Change	Water Drained Off Cc.	Acid per 0.01 *N* 100 Cc. Cc.	Acid Removed Cc.	Acid per 100 G. Dry Cc.
1	2000	339.2	6796	6700
2	2000	76.8	1536	1520
3	2000	36.9	736	729
Total acid removed			9070	8949

Residual Acidity Left by Water

Inside titration 2 g. dry	29.26 cc. 0.01 *N*
Acid left per 100 g. dry	1464 cc.
Total acid per 100 g. dry	10,413 cc.
Per cent acid not removed	14.02

---

[1] Compare Cross and Luck's method with 10 per cent acetone, *J. Soc. Chem. Ind.*, **19** (1900), 642.

[2] See *Koll. Z.*, **27** (1920), 209, 223, for a recent presentation.

[3] *Loc. cit.*, 106

[4] That is, subtractive stabilization.

[5] *E. g.*, as expressed by Robertson, *Loc. cit.*

[1] Alkalinity equivalent to 1 cc. 0.1 *N* per 100 cc.

[2] Schrimpff, *Loc. cit.*

"SULFATE" LEACH PULPING

Nitrocotton No. 578........................Short fiber
Weight of soused nitrocotton..................600 g.
Weight of moist pulp........................261 g. drained
Weight of dry pulp .... 111.3 g.
Leach changed 3 times in 24 hrs.

Alkalinity of Leach = 12 cc. 0.01 *N* per 100 cc.

No. of Change	Liquid Drained Off Cc.	Acid per 0.01*N* 100 Cc. Cc.	Acid Removed Cc.	Acid per 100 G. Dry Cc.
1	2000	453.9	9030	8130
2	2000	370.8	7420	6670
3	2000	41.55	831	746
	Total acid removed.........		17281	15546

Residual Acid Left by Sulfate Leach

Inside titration 2 g. dry........................7.2 cc. 0.01 *N*
Acid per 100 g. dry........................360 cc.
Total acid per 100 g. dry...................... 15,906 cc.
Per cent acid not removed........................2.32

It will be seen that though the total acidity was considerably higher[1] in the sample used for sulfate pulping the removal of acid, though incomplete with only three leaches, was much better than with "hard" water, only 2.3 per cent of the total acidity being left, as compared with 14 per cent for water. The actual acidities per 1 g. dry were:

1 g. dry, by water	14.7 cc.
1 g. dry, by sulfate	3.6 cc.

One important conclusion from these experiments is this. Although, as already stated, the same degree of mechanical subdivision is reached earlier in water than in sulfate, the acid removal lagged behind that by sulfate. *It appears evident that merely mechanically shortening and destroying the fibers does not greatly facilitate acid removal*, beyond its effect in assisting uniform penetration of large masses. In spite of the fine subdivision of the nitrocotton (see Fig. 9) the latter portions of acid are obstinately retained in water by pulped nitrocotton. In fact, the increased dispersity probably increases this retention, in consequence of the greater surface developed. This acid is, however, readily removed by sulfate leach. This tends to confirm our view that the residual acid is held by selective adsorption, not by mechanical occlusion, and that the sulfate leach acts osmotically on the membrane structure of the fiber primarily, and only secondarily on the cell.

It further appears from these results that if pulping or disintegrating were combined with a sulfate leaching process this would be most desirably effected after acid boiling, stabilizing, leaching out of acid, and washing out of sulfate. Actually, this would correspond with the usual practice where pulping is employed, both for guncotton and for celluloid.[1] Where final boiling in weak alkaline solutions is desired for guncotton, this could be initially effected after pulping in the weakly alkaline water, as this assists the disintegration. In the celluloid industry it is very general to bleach the nitrocellulose after pulping.

We have tested various bleaching methods on sulfate treated cotton, *e. g.*, permanganate followed by bisulfite, "chloride of lime" bleach, sodium hypochlorite, chlorine gas, and hydrogen peroxide, and find them to act at least equally as well on sulfate-leached cotton as on water-washed. Hence, neither the introduction of pulping, nor of pulping and bleaching offers difficulty in the installation of a purification régime utilizing the sulfate leach as the essential deacidifying process.

ACKNOWLEDGMENT

The writer desires to express his thanks to Mr. W. H. Davis for continued assistance in the experimental work, and to Messrs. A. Armstrong and P. Seel of the Chemical Plant for their coöperation in large-scale trials.

The Production of Furfural by the Action of Superheated Water on Aqueous Corncob Extract[2]

By **F. B. LaForge**

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

In a recent paper on the preparation of corncob adhesives by the hydrolysis of field corncobs with hot water under pressure, it was noted that a certain amount of furfural was always produced.[3] In the present paper a description is given of a method for treatment of corncobs in such a way that the cellulosic material can be obtained and, in addition, an amount of furfural corresponding to 7.76 per cent of the weight of the original cobs.

The method consists in heating the cobs under pressure for a short time with hot water, a procedure which does not injure the cellulosic material. An amount of furfural corresponding to about 2.8 per cent of the weight of the cobs is formed at the same time and is blown off with a certain amount of water when the pressure is released. The crude cellulosic residue is filtered and pressed, and the aqueous liquors, which contain a considerable amount of soluble carbohydrates, are heated with water under pressure, thus causing hydrolysis and formation of a further amount of furfural, sufficient to make a total weight of 7.76 per cent of the original cobs.

A comparison of this process for the production of furfural with those now described in the literature indicates certain advantages for the former. Not only is the cellulose saved, but the process has the great advantage of using only water for hydrolysis in place of acid. Moreover it will be noted from the experimental results that the time necessary for handling a given amount of cobs is shorter than is customary by the methods so far described using acid hydrolysis. The method can also be applied to the preparation of furfural from corn husks, corn stalks, and bagasse, and probably from many other plant materials rich in pentosans.

EXPERIMENTAL

One kilo of cobs was heated in an autoclave of about 6-l. capacity with 4000 cc. of water at 180° to 185°. After this temperature had been maintained for three-quarters of an hour, the pressure was released and the vapors were allowed to pass through a condenser. The amount of condensate thus collected was 815 cc. Since 5 cc. of this condensate gave (*a*) 0.3268 g., (*b*) 0.3255 g. of phloroglucide, 815 cc. contained 28.0 g. of furfural. The cellulosic residue remaining in the autoclave was filtered with pressure, and 2650 cc. of filtrate containing soluble carbohydrate material capable of further hydrolysis to furfural were obtained. The cellulosic residue was washed with 2000 cc. of water, pressed again, and set aside for other purposes.

The filtrate obtained from the washings was diluted to 4000 cc. with water and used for heating a second batch of 1 kg. of cobs under the conditions given above. In the same way, 825 cc. of distillate were obtained, which contained about 28 g. of furfural. The cellulosic material was filtered by pressure and washed with 2000 cc. of water, and again pressed. The filtrate and wash waters from this second kilo of cobs were mixed and concentrated to their original volume of 3175 cc. (the 4000 cc. minus 825 cc. blown off when the pressure was released). This solution, with the 2650 cc. obtained from the first kilo of cobs, contained the carbohydrate material from 2 kg. of cobs.

---

[1] It is almost impossible to obtain uniformity in this respect in small samples of "soused" nitrocotton.

[2] Presented before the Division of Organic Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[3] *Chemical Age (N. Y.)*, **28** (1920), 332; see also *Z. angew. Chem.*, **27** (1914), 654; THIS JOURNAL, **13** (1921), 133.

[1] Schrimpff, *Loc. cit.*, 96

Forty-five hundred cc. of this solution, which represented the soluble extracts from 1540 g. of cobs, were heated in the autoclave at 180° to 185°. After 15 min. the autoclave was blown off through the condenser as before. The amount of condensate was noted and an equal volume of water was added to the contents of the digester and it was again heated for 15 min. at 180° to 185°. This was then blown off, the volume of the condensate noted, an equal volume of water added to the digester, and the heating repeated. This was carried out five times, after which so little furfural was being produced that it was not worth while to carry the process further.[1] The following table denotes the results obtained by five successive heatings of 4500 cc. of soluble extractives obtained by the method described above.

No.	Condensate Cc.	Phloroglucide G. from 5 Cc.	Furfural G. in 5 Cc. (Av.)	Furfural in Condensate Grams	Furfural in Condensate Per cent
1	750	(*a*)0.2770 (*b*)0.2738	0.1454	21.8	2.91
2	775	(*a*)0.2610 (*b*)0.2625	0.1383	20.9	2.70
3	755	(*a*)0.2137 (*b*)0.2180	0.1146	17.3	2.29
4	725	(*a*)0.1310 (*b*)0.1240	0.0691	10.2	1.38
5	725	(*a*)0.0752 (*b*)0.0760	0.0420	6.1	0.84

If it is desired merely to prepare furfural and not to save the cellulose, the process could be made continuous from the start, following the general procedure just described for the hydrolysis of the soluble carbohydrate extractives. Under these conditions the cellulosic material would be allowed to remain in the digester during the complete process. It should be emphasized, however, that the cellulose may have as great value as the furfural in technical operations and it is of great importance to preserve it from injury by overheating.

The Color Value of a Tan Liquor as a Function of the Hydrogen-Ion Concentration[2,3]

By **John Arthur Wilson and Erwin J. Kern**

Laboratories of A. F. Gallun & Sons Co., Milwaukee, Wisconsin

In judging the value of a vegetable tanning extract, tanners often place much weight upon the color imparted to skin by solutions of the extract. This has given rise to a movement to try to devise some satisfactory method for measuring the color value of an extract. In Europe the tendency has been toward matching a solution of the extract with standard colored glasses, but apparently the preparation of absolutely standardized glasses is a serious problem. Moreover, the color of a tan liquor is not necessarily a measure of the color it will give to a skin. In this country preference seems to have been given to a method involving the observation of the color of strips of sheep or calf skin tanned in a standard solution of the extract. A strip of tanned skin accompanying the analysis report is apt to find greater favor with the tanner than figures on an arbitrary scale, but this method has sometimes been deceptive, because a given tan liquor may impart different colors to samples of skin from different sources. The present paper does not deal with the question of measuring color values, but with factors powerfully affecting such measurements which in the past have been uncontrolled and apparently often quite unappreciated.

It has long been known that the presence of lime in a tanned skin will cause a darkening of the color. If the skin is treated with mineral acid soon after tanning, the color brightens, but the effect of acid becomes less pronounced the longer the skin is previously allowed to stand exposed to air. In our studies on the effect of change of hydrogen-ion concentration upon tanning, we obtained leather differently colored for each different pH value of the tan liquor. It was immediately apparent that the color of a tan liquor as well as that of the leather is a function of the hydrogen-ion concentration.

INDICATOR EFFECT

Two tan liquors were prepared, one from gambier and the other from quebracho extract. To each was added sufficient phosphoric acid to bring the pH value to 2.5, as determined by the hydrogen electrode. The phosphoric acid was added to act as a buffer in preventing large changes in pH value upon long standing. To equal portions of each, sodium hydroxide was added to give series of tan liquors ranging in pH value from 3.0 to 12.0 and all having a tannin content of 1 per cent, as determined by the authors' new method.[1] The gambier series varied in color from light straw at pH = 3.0 to a very deep red at 12.0. The quebracho series was similar in color excepting that the liquors of lower pH value had a touch of violet. Either series resembled a standard series of colors used in the indicator method of determining hydrogen-ion concentration, except for the fact that a light precipitate formed in all liquors having a pH value of 4.0 or less. The difference in color was evidently a true indicator effect, for any member of the series could be made to match any other member simply by bringing it to the same pH value. All members of either series appeared practically identical when brought to a pH value of 3.0. This complete reversibility of color change, however, was not found when liquors at higher pH values were allowed to stand long exposed to air.

OXIDATION EFFECTS

Two complete series of each extract were poured into test tubes; the tubes of one series of each were tightly stoppered, while the others were left uncovered. Next day the liquors in the stoppered tubes showed practically no change, but the others had become darker in color, the more so the higher the pH value. When the liquors in a series not exposed to air were all brought to a pH value of 3.0, they all assumed practically the same color. But when those of a series that had been exposed to air were all brought to 3.0, they did not assume the same color, but were darker the higher the pH

---

[1] In large-scale practice the process may be made continuous by keeping the temperature constant and maintaining a constant level in the digester by continuous addition of water or steam.

[2] Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[3] Received August 22, 1921.

[1] THIS JOURNAL, 12 (1920), 465, 1149.

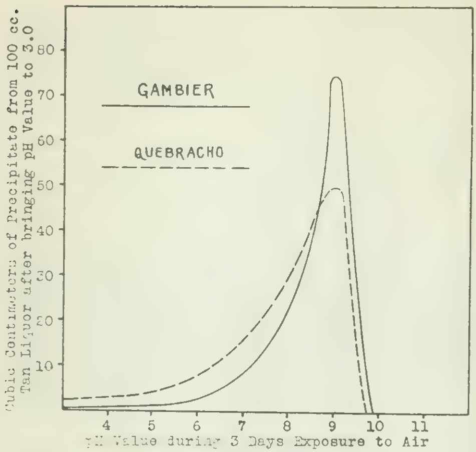


Fig. 1—Showing How Tendency of a Tan Liquor to Form a Precipitate When Brought to a pH Value of 3 Varies with Its pH Value during a Period of Exposure to Air

value during the period of exposure to air; furthermore a precipitate settled out from those whose pH values had been in the vicinity of 9.

This precipitate formation is very curious. A complete series of each extract was allowed to stand exposed to air in shallow dishes for 3 days; the liquors were then made up to original volume and poured into 100-cc. graduate cylinders. Each was brought to a pH value of 3.0 by the addition of hydrochloric acid and allowed to stand over night. Next day the volume of precipitate from 100 cc. of original liquor was read from each cylinder. The results are shown in Fig. 1. Keeping a solution of either extract exposed to air while its pH value is 9 causes it to yield an enormous precipitate when its pH value is subsequently brought to 3.0. But keeping it exposed to air when its pH value is greater than 10 apparently prevents its precipitation when brought to 3; all such liquors remained brilliantly clear. The addition of a great excess of acid, however, caused all liquors to precipitate, while any precipitate could be completely redissolved by the addition of sufficient alkali.

Another interesting fact is that the liquors exposed to air when their pH values lay between 8 and 9 gave much trouble with the hydrogen electrode. After bubbling hydrogen through them for only a few minutes, the voltage would fall rapidly towards zero. Even when brought to a pH value of 3.0, the liquors still gave this trouble and we had to check the results by means of indicators. No such trouble was encountered with liquors exposed to air at pH values below 7 or above 10. Apparently pH = 9 is a critical point in the oxidation of tan liquors. It may prove valuable to make much more extended studies of the changes going on at this point.

Effect upon Leather

The changes in color of the tan liquors parallel in a rough way the changes in color imparted to hide. A hide tanned in a liquor having a high pH value not only comes from the liquor very dark in color, but this color continues to darken upon exposure to air.

Summary

The color value of a tan liquor depends upon its hydrogen-ion concentration when used. A change in pH value produces a change in color of both liquor and leather.

Tan liquors change in color like indicators with change in pH value, but over a range from 3 to 12. This change in color is completely reversible, if the liquors are not long exposed to air.

Liquors exposed to air continue to darken in color, the more so the higher the pH value, but this change is not reversed by lowering the pH value. Liquors exposed to air at pH values of about 9 give bulky precipitates when their pH values are brought to 3, and such liquors tend to poison the hydrogen electrode.

The Tannin Content of Pacific Coast Conifers[1]

By R. H. Clark and H. I. Andrews

Department of Chemistry, University of British Columbia, Vancouver, Canada

This investigation was made to determine how the tannin content of western hemlock (*Tsuga heterophilla*) and spruce (*Sitka*) bark varies with the month of the year in which the tree is cut. The samples of bark were taken from trees, either standing or just felled. In no case had the logs been in the water. Samples for nine months of the year were analyzed for total solids, solubles, non-solubles, tannins, non-tannins, and moisture. The bark came from Kingcome Inlet, B. C., from the vicinity of Kingcome River. As nearly average a sample as possible was sent from the woods.[2] The samples for the months of May and June were held about 2 mo., in stoppered bottles, before the analyses were made; the effect of such seasoning might possibly have raised the tannin content slightly, as the effect of seasoning douglas fir was found by Benson and Jones[3] to be. All values recorded are the average of two separate extractions.

The extraction and analyses were carried out by the standard methods of the International Association of Leather Trades' Chemists, as described by Lunge and Keane.[4]

The average sample shipped from the woods weighed about 4 lbs. This was resampled, and about 300 g. were ground up in an ordinary meat chopper until it all passed through a 20-mesh sieve. In most cases 25 g., in some 20 g., of the ground bark were extracted, as this amount was found to give the required 3.5 to 4.5 g. of tanning material per liter. The extract from all the bark was quite clear and remained so for some time, with the exception of a few spruce samples, which deposited a very slight precipitate.

The total solids were determined by drying 100 cc. of the extract at 100°. The total solubles were found by evaporating 100 cc. of the extract which had been filtered through a Berkfeld filter until the filtrate was clear by the reflected and transmitted light of an electric lamp. The first 200 to 300 cc. of filtrate to pass through the filter was rejected, to avoid any correction for absorption. The tannin was determined by shaking the extract in a mechanical shaker with hide powder, previously tested and chromed. A clear solution of the non-tannins was left, which was evaporated, and the non-tannins weighed. The tannin absorbed by the hide powder is given by the difference between the total solubles and the non-tannins.

In the case of hemlock, the tannin content rises quite

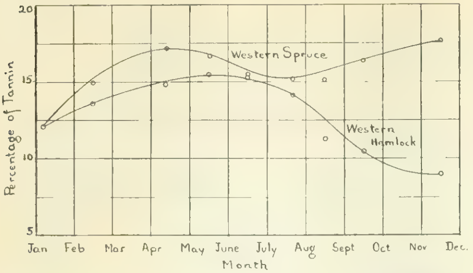
---

[1] Received June 6, 1921.

[2] We wish to thank the Powell River Co., Ltd., for their kindness in providing the samples.

[3] This Journal, 9 (1917), 1096.

[4] "Technical Methods of Analysis," Part I, Vol. III.



Month Cut	Tannin Content Total Solids	Tannin Content Solubles	Tannin Content Insolubles	Calculated (Bone-Dry) Tannins	Calculated (Bone-Dry) Non-tannins
		Western Hemlock			
January 5	18.44	17.78	0.66	12.05	5.73
February 14	20.27	19.64	0.63	13.66	5.98
April 12	22.10	21.66	0.45	14.84	6.82
May 15	22.96	22.28	0.68	15.50	6.78
June 15	22.30	21.70	0.60	15.30	6.40
July 20	20.50	19.16	1.34	14.15	5.01
August 15	15.98	15.48	0.50	11.34	4.14
September 15	14.88	14.57	0.31	10.52	4.05
November 15	12.96	12.89	0.07	9.00	3.89
		Western Spruce			
January 5	18.11	17.23	0.88	12.01	5.22
February 14	24.78	23.64	1.14	14.96	8.68
April 12	26.38	24.89	1.48	17.19	7.70
May 15	26.81	24.60	2.22	16.58	8.02
June 15	24.58	22.72	1.86	15.46	7.25
July 20	24.74	22.72	2.02	15.24	7.48
August 15	22.56	21.09	1.47	15.10	5.99
September 15	22.39	20.79	1.60	16.39	4.40
November 15	27.44	25.30	2.14	17.54	7.76

regularly during the first six months of the year and then declines. For spruce, however, a similar regularity was not found; there appears to be a maximum in the spring of the year, then a gradual falling off with another maximum in the late fall. The accompanying curves show the tannin content in per cent, on a bone-dry basis, plotted against the time of the year in which the sample was collected.

The tannin value found for hemlock is somewhat less than found for Western hemlock bark from the State of Washington by Dr. H. W. Wiley and also H. G. Tabor and referred to by Professor H. K. Benson.[1] Very few references to the tannin content of spruce could be found, the results obtained throughout were higher than expected, especially so, when compared with the results obtained by Professor Benson on a sample of sawmill bark, the history of which was unknown. The tannin content is known to be affected by many factors, among them being the length of time the log is floated in water, by how much of the cambium layer is taken with the sample, and probably by the age of the tree and length of seasoning.

Summary

The tannin content of freshly cut western hemlock (*Tsuga heterophilla*) bark varies from 9 to 15.5 per cent, according to the month of the year the sample is taken and averages, for the 9 mo. investigated, 13 per cent; that of spruce (*Sitka*) varies correspondingly from 12 to 17.5 per cent with the season, and averages about 15.6 per cent.

It would appear that the extraction of tannin from the bark from the pulp and paper industries of British Columbia should be profitable.

The Alkaline Hydrolysis of Casein[1]

By Mary A. Griggs

Department of Chemistry, Wellesley College, Wellesley, Massachusetts

It is the general belief that hydrolysis of proteins by acids gives the most satisfactory products for a study of the composition of the protein molecule or for the isolation of the different amino acids. In certain processes, however, where amino acid mixtures are required for chemical uses, such as the production of chloramines, or for the nutrition of bacteria, molds, etc., the usual methods of acid hydrolysis are not desirable because of the special apparatus required. Since alkaline hydrolysis of proteins can be carried out in iron or steel vessels and the products of the hydrolysis readily recovered, this method can often be used with advantage. Although alkaline hydrolysis promotes the racemization of optically active amino acids, this is not ordinarily a serious consideration. In view of the scarcity of data relating to the conditions most favorable for alkaline hydrolysis, it became necessary in connection with a larger problem to study the changes in the hydrolysis of a characteristic protein, casein, caused by variations in time of hydrolysis and in concentration of alkali, within certain limits.

Abderhalden and Brahm[2] found that a residue from the hydrolysis of Shantung silk which was not hydrolyzed further either by concentrated hydrochloric acid or by 25 per cent sulfuric acid gave a considerable yield of alanine when treated with 33 per cent soda lye. Abderhalden, Medigreceanu and Pincussohn[3] studied the hydrolysis of silk by hydrochloric acid (1.2 sp. gr.), 25 per cent sulfuric acid, 25 per cent sodium hydroxide, and saturated barium hydroxide, and concluded from repeated experiments that, within narrow limits, equivalent mixtures of amino acids were obtained whether acids or alkalies were used for the hydrolysis of the silk. Van Slyke[2] used casein, among other proteins, in determining the conditions for complete hydrolysis by acid. These experiments showed that the amino nitrogen reaches a definite maximum at which the hydrolysis by acids is complete and that this maximum does not vary whether the temperature of the experiment is 100° or 150°. The yield of amino nitrogen is also the same whether the protein is boiled for 24 hrs. with 20 per cent hydrochloric acid or heated in an autoclave at 150° for 1.5 hrs. with 10 per cent hydrochloric acid. The yield of amide nitrogen increased quite regularly with the time and temperature of the hydrolysis.

The present work on the hydrolysis of casein by sodium hydroxide also showed the usual maximum yield of amino nitrogen, but in this case the maximum varied considerably with the concentration of the alkali and appeared much more quickly with the more concentrated solutions. The yield of amide nitrogen found was irregular owing to the volatilizing of ammonia from the alkaline solution, but in general it increased with the time of hydrolysis.

Experimental

The material used was a sample of natural-sour casein.

The hydrolysis was carried on in an autoclave immersed in an oil bath at ±150° C. The time was reckoned beginning when the temperature of the contents of the autoclave reached 150°. The casein was added to the cold water while it was being stirred vigorously, to prevent lumping, and the dissolved alkali was then added, and the whole thoroughly stirred before it was transferred to the autoclave. After hydrolysis, the autoclave was allowed to cool before it was opened. A filtered portion was then distilled into standard sulfuric acid for the determination of ammonia.

---

[1] This Journal, 7 (1915), 915.

[1] Received June 8, 1921.

[2] *Z. physiol. Chem.*, **61** (1909), 256.

[3] *Ibid.*, **61** (1909), 205.

[2] *J. Biol. Chem.*, **12** (1912), 295.

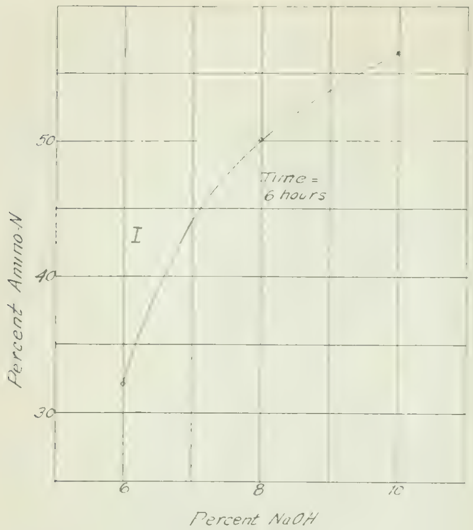


FIG. 1

This method of handling the alkaline solution necessarily gave inaccurate results for ammonia. The solution thus freed from ammonia was used for the determination of amino nitrogen by the Van Slyke method.[1] The per cent of amino nitrogen on the basis of the total nitrogen content was calculated, using the average nitrogen content of casein, 12.7 per cent. One hundred grams of casein in a volume of 500 cc. were used in each determination. The hydrolysis when 30 g. sodium hydroxide were used was so incomplete after 6 hrs. that further tests were not made. Forty grams of sodium hydroxide carried the hydrolysis much further, and experimental runs were made covering its use for a number of different periods. Fifty grams of sodium hydroxide gave a higher maximum in a shorter period and the use of this amount was similarly tested until the maximum was passed. The curve, Fig. 1, indicated that still higher concentrations of alkali would not be worth while, so no further series of experiments were tried.

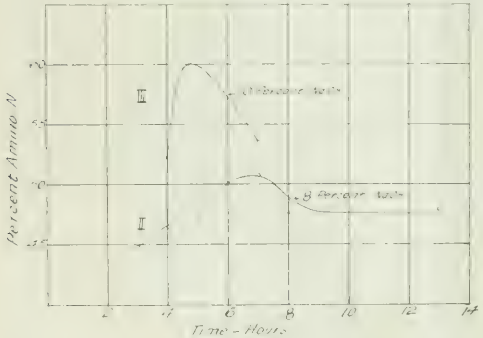


FIG. 2

SUMMARY

The following results show that when the hydrolyzing solution contains 6 per cent by weight of sodium hydroxide only a low yield of amino nitrogen is obtained. When the concentration is increased to 8 per cent, the yield of amino nitrogen is greatly increased, while a further increase in concentration to 10 per cent shows only a few per cent more amino nitrogen. The maximum yield with 10 per cent sodium hydroxide is 10 per cent higher than with 8 per cent sodium hydroxide and is attained about 2 hrs. earlier.

TABLE I—VARIATION IN YIELD OF AMINO NITROGEN WITH CONCENTRATION OF ALKALI

Casein Grams	NaOH Concentration Per cent	Time Hours	Amino Nitrogen Grams	Amino Nitrogen Per cent of Total Nitrogen
100	6	6	4.052	31.91
100[1]	8	6	6.358	50.07
100	10	6	7.175	56.50

[1] Calculated by interpolation from Curve III.

TABLE II—RELATION BETWEEN YIELD OF AMINO NITROGEN AND TIME OF HYDROLYSIS

Casein Grams	NaOH Concentration Per cent	Time Hours	Amino Nitrogen Grams	Amino Nitrogen Per cent of Total Nitrogen
100	8	3	5.698	44.86
100	8	4	5.913	46.55
100	8	5	6.008	47.31
100	8	6	6.358	50.06
100	8	7	6.438	50.68
100	8	8	6.164	48.54
100	8	8	6.040	47.55
100	8	9	6.020	47.40
100	8	13	6.080	47.88
100	10	4	6.629	52.20
100	10	4.75	7.623	60.03
100	10	7	6.817	53.66

Accordingly the optimum method is to use 10 per cent sodium hydroxide for the hydrolysis of casein and to run the process 5 hrs.

The author plans to extend this investigation to other proteins in the chemical laboratory at Wellesley College.

ACKNOWLEDGMENT

The author wishes to express to Professor Ralph H. McKee of Columbia University her appreciation of the opportunity given by him to do this work in his private laboratory, and to Dr. Edward M. Frankel her gratitude for his suggestions, interest, and assistance in this work.

Malt Extracts and Shortening Agents Registered by American Institute of Baking

Definite progress is being made by the American Institute of Baking in the examination and registration of baking materials. *Bulletin* **6** issued by the Institute in September contains a list of fifty malt extracts and shortening agents which have been tested and approved by the Institute. The right is reserved to cancel certificates of registration whenever it is apparent that the character of the registered article no longer entitles it to favorable recognition, and in such cases the baking industry will be fully informed by the Institute. Additional lists of registered products will be published by the Institute from time to time and bakers are asked to assist in the work by submitting for examination all new products which may be offered them. Manufacturers are also asked to submit their products for examination.

On and after November 1, the Institute will receive applications and samples for registration from manufacturers of milk products and special preparations which may be classified as "yeast foods" and "bread improvers." The examination of the latter class of products will not cause a discontinuance of the examination of shortening agents and malt preparations. It is also expected that the scope of examinations and registrations will be extended to other articles used in baking as soon as this is feasible.

In *Bulletin* **6** it is stated that the Institute is making no attempt to classify the products examined from the standpoint of comparative value. The object of the examination is primarily to establish the statements of the manufacturer as to composition and claims. The actual choice of a particular brand of an article used in baking is a matter governed by economic and practical considerations, provided of course that the products have passed the standard tests.

Experiments with the growing of the chaulmoogra tree at the United States plant introduction garden near Chico, Cal., are being conducted with a view of determining the expediency of producing chaulmoogra oil from American grown trees instead of depending on India for this valuable medicinal product.

---

[1] *J. Biol. Chem.*, **12** (1912), 275.

Volume Increase of Compounded Rubber under Strain[1]

COMMENTS ON AN ARTICLE BY H. F. SCHIPPEL[2]

By Henry Green

Research Laboratory, New Jersey Zinc Co., Palmerton, Pa.

This discussion is not intended as a criticism on Mr. Schippel's work. It was written expressly for the purpose of offering a suggestion, to those interested in the subject of "volume increase," as to a method of studying this phenomenon not specifically mentioned in Mr. Schippel's paper. The following excerpt will be sufficient to present the idea involved:

> While studying the nature of the stress-strain curves for rubber containing different pigments in varying quantities, the writer [H. F. Schippel] considered the stability of the rubber surrounding each particle of pigment in the rubber body, and thought that possibly when the rubber body was elongated sufficiently the rubber might pull away from the particles of pigment in their axes of stress and cause vacua to be formed on both sides of each particle, the net result of which would be a considerable increase in the volume of the rubber body as a whole.
>
> A preliminary test was made by preparing a transparent vulcanized compound containing a fair proportion of medium-sized lead shot. When this compound was stretched, the formation of vacua proceeded gradually until each lead shot had its conical vacua on both sides in the direction of strain. This was very satisfactory and the test was immediately applied to miscellaneous samples of rubber compounds, with the result that this integral phenomenon was actually found to take place.

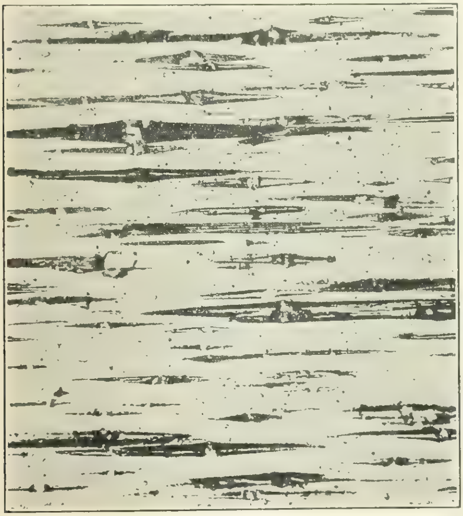


Fig. 1—Stretched Rubber Containing Barytes, Showing "Vacua" at Ends of Particles and Extending in the Direction of Strain. Magnification 200 Diameters

From the last sentence it is somewhat difficult to decide whether shot was introduced in the rubber compounds and the vacua observed in connection with that material, or whether the vacua appeared at the ends of the miscellaneous pigments which presumably were also present in these rubber compounds.

It seemed to the author that, if this last condition was the one implied, Mr. Schippel would naturally have made some reference to a microscopic examination, since otherwise these minute vacua could not have been shown to exist. As no such reference appeared in his paper, the author believed that it would be both interesting and novel to eliminate the shot, introducing in its place a material like ground barytes, and to observe microscopically the conditions arising during subsequent stretching of the rubber compound.

Experimental Details

Rubber sheets approximately 0.01 in. in thickness containing the barytes which it was desired to study were prepared. These sheets were cut into strips 3.5 in. × 0.25 in. in dimension. One end of a strip was fastened to a microscope slide by means of sealing wax. After the solidification of the wax the rubber was stretched to the desired percentage elongation and the strip fastened at the other end of the slide. A suitable mounting medium such as glycerol or cedar oil was then allowed to flow under the strip and some also placed on the upper side. After placing a cover glass upon this, the specimen was ready for examination.

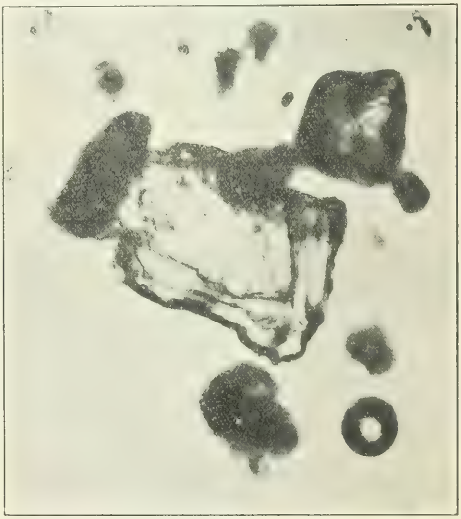


Fig. 2—Unstretched Rubber, Compounded with Barytes. Magnification 1500 Diameters

(The large particle in the center is the only one present which is in close contact with the rubber; the others are surrounded by a film of gas and will, therefore, produce "vacua." The particle in the lower right hand corner appears to be a bubble. There is actually a particle present, however, as was revealed by closer focusing.)

The result is shown in Fig. 1. The barytes particles are clearly shown with conical vacua at the ends, extending in the direction of elongation. The clear white field is the pure rubber containing a large number of small barytes particles which evidently have produced no vacua.

The experiment was modified as follows: The rubber strip was fastened to the glass slide at one end only, and the specimen was placed on the microscope (which was equipped with a mechanical stage), and slowly stretched. As the elongation

---

[1] Presented before the Division of Rubber Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] This Journal, **12** (1920), 33.

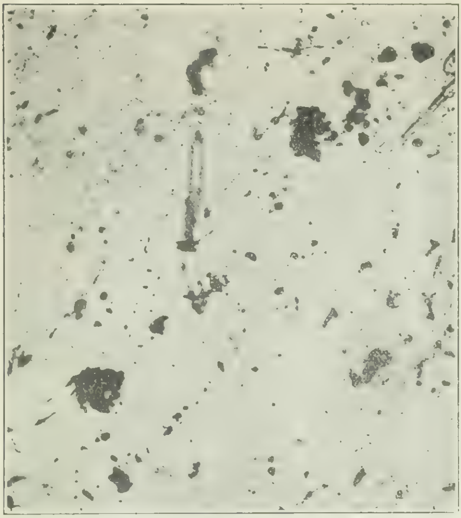


FIG 3—UNSTRETCHED RUBBER CONTAINING "AGGLOMERATED MASSES" OF PIGMENT. EACH BLACK SPOT IS COMPOSED OF PERHAPS THOUSANDS OF PARTICLES

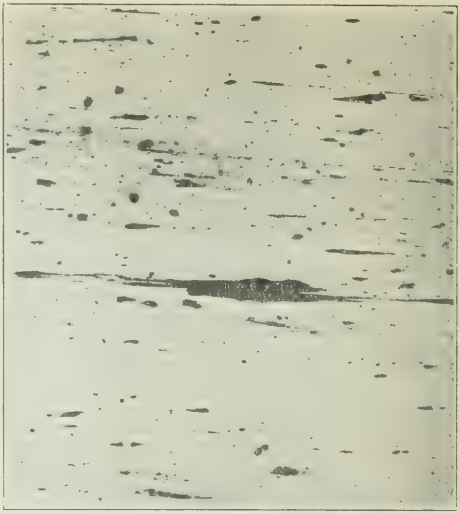


FIG 4—SAME RUBBER SHOWN IN FIG. 3, IN A STRETCHED CONDITION NOTICE THAT THE AGGREGATES ARE SOFT AND EASILY DEFORMED INTO LONG STREAKS

increased the stage was moved in the opposite direction so that any individual particle of barytes could be made to remain in the field during observation. In this way the actual formation of the vacua could be studied. It was noticed that certain particles invariably formed vacua, while with others it was almost impossible to produce them. The reason for this fact is probably explained in Fig. 2. Of the eleven largest particles present the white one in the center is the only one in close contact with the rubber. (As in the preceding figure the clear field is the rubber in which the barytes is imbedded.) The other particles are surrounded by a gaseous film, which on account of its low index of refraction causes the particles to appear dark. It is hardly necessary to state that the so-called "vacua" will be formed in this latter case, while with the large particle in the center the result cannot safely be predicted.

Finer pigments than barytes have also been investigated by this method. For materials as fine as zinc oxide, carbon black, etc., a 2-mm. oil immersion objective and a magnification preferably of 1500 diameters are required. The cover glass is dispensed with and the objective immersed directly in the mounting fluid. So far, the results of experiment have indicated that no vacua are formed with fine pigments when compounded in small percentages. This naturally leads to the point discussed by Mr. Schippel in regard to the effect produced by agglomerated masses on volume increase. Where the percentage of pigment is high, aggregation is more likely to be present, and it was suggested that if aggregated masses tended to augment the volume on extension, it would be easily understood why highly pigmented rubber possessed this property to such a marked degree.

THEORETICAL DISCUSSION

At first glance this conclusion seems so obvious that further discussion would be unnecessary. On closer analysis, however, it is not quite so self-evident why agglomerated masses tend to cause volume increase when subjected to elongation.

If any fine-grained powder be examined microscopically it will be found to be composed of small soft pellets. Microscopic examination of these pellets will further reveal the fact that they are in turn composed of perhaps many thousands of individual particles. A pellet then is an agglomerated mass. If such a pigment is not thoroughly incorporated in a compounded rubber these masses will exist intact. (Fig. 3.) The immediate problem now is to determine whether or not there is any change in the volume occupied by these pellets when the rubber is stretched. (Fig. 4.)

It is apparently an accepted fact that there is no measurable change in the volume of pure unpigmented rubber upon extension. Granting this to be so, it then follows that if a solid rubber cylinder (Fig. 5) is stretched to n times its length, its circular cross-section will be reduced to $1/n$ times its original area. In other words, the radius has been decreased from R to r where $r = \frac{R}{\sqrt{n}}$.

Let us now suppose that in the center of this cylinder, tangent to its walls, there should be a vacuous spherical cavity and that the cylinder itself is placed in a vacuum. The volume of such a cavity will be

$$V = 4/3\pi \; a \times a \times a$$

where a is its radius. Let the cylinder now be stretched to n times its length; then the volume of the deformed cavity

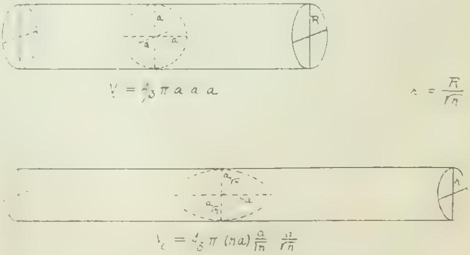

a
a
a
R
$V = \frac{4}{3}\pi a \; a \; a$
$r = \frac{R}{\sqrt{n}}$
$\frac{a}{\sqrt{n}}$
a
$\frac{a}{\sqrt{n}}$
r
$V_t = \frac{4}{3}\pi \,(na) \frac{a}{\sqrt{n}} \; \frac{a}{\sqrt{n}}$

FIG 5—MATHEMATICAL MODEL DEMONSTRATING THE INVARIABLE VOLUME OF A SPHERICAL CAVITY IN RUBBER, DURING THE PROCESS OF STRETCHING

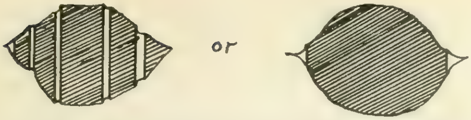


FIG 6—MODEL OF AGGLOMERATED MASSES OF PIGMENT WHEN STRETCHED, ILLUSTRATING PROBABLE CONDITION WHICH PRODUCES "VOLUME INCREASE"

will be the volume of an ellipsoid of revolution about the axis of elongation and will be equal to

$$V_e = 4/3\ \pi\ (na)\ \frac{a}{\sqrt{n}}\ \frac{a}{\sqrt{n}}$$

$$\text{or } V_s = V_e$$

That is, there is no change in the volume of the cavity when the rubber is stretched.

If this cavity were filled with a gas at a given pressure, and the rubber stretched adiabatically, it necessarily follows that there can be no change in volume as a result thereof, though of course we are now dealing with a larger volume (due to gas pressure) than was the case when the cavity was empty.

If, instead of a gas-filled cavity, we should have one completely occupied by a pellet of pigment (an agglomerated mass), it is not so evident just why there should be volume increase upon stretching.

In the empty cavity, as already stated, there can be no increase in volume. Any form of material placed in the cavity that would cause such a condition to take place upon stretching, would have exerted upon it, by the walls of the cavity, a compressive force acting in the opposite direction. As a gas is a fluid it must obey the viscous law, that is, an infinitely small force will cause it to flow. If then, at any time during stretching, the gas should exert an extensive action it will be met by an equal and opposite compressive force which will be completely used in molding the gas into its new form. On the other hand, a pellet of powder, being similar to a plastic material, will require the application of a finite force of definite magnitude, before it undergoes a change in shape. As such is the case, all of the compressive force is not utilized, and there will exist a residual quantity of it equal to the previously mentioned finite force necessary to cause the aggregate to flow. *The presence, therefore, of this small quantity of force implies that there has been a volume increase.* Fig. 6 is an attempt to visualize this condition. The white sections in this figure represent air spaces; the shaded ones, a mixture of pigment and occluded air. It should be understood that the figure is only a theoretical model never attained in practice. The air spaces would be extremely minute and overlap in such a manner that to detect them with a microscope would be impossible.

CONCLUSION

Theoretically, at least, Mr. Schippel's contention that agglomerated masses of pigment are responsible for a part of the volume increase, is justifiable. Whether or not this evidently small volume increase is sufficient to account for the quantity found experimentally, will be difficult to decide. No doubt there are other forms of aggregation, such as very small ones like doublets, which upon extension will produce sufficient volume increase to explain fully Mr. Schippel's interesting discovery.

Discussion of the Tetrabromide Method for Estimating Rubber Hydrocarbon[1]

By Harry L. Fisher, Harold Gray and Ruth Merling

RESEARCH LABORATORIES, THE B. F. GOODRICH CO., AKRON, OHIO

The tetrabromide method is the oldest method for estimating rubber hydrocarbon. As originally described[2] it consisted of the preparation of the rubber tetrabromide in solution, precipitation with alcohol, washing and drying, and determination of the bromine in the product. Several modifications followed, mostly in the methods of preparation and of determination of the bromine in the precipitated sample. The latest modification of the method has been made by W. K. Lewis and W. H. McAdams,[3] who have applied the method of McIlhiney[4] for the estimation of unsaturated oils by means of bromine in an organic solvent. Briefly, the rubber is dissolved in carbon tetrachloride and treated with a solution of bromine in the same solvent. After standing from 2 to 4 hrs. the excess of bromine is titrated with sodium thiosulfate after the addition of a solution of potassium iodide, using starch as the indicator. Since substitution always takes place, as shown by the presence of hydrogen bromide, the amount of bromine used, as determined by titration, does not give the correct figure for the amount actually added to the double bonds. This is remedied by immediately adding some potassium iodate solution which converts the hydrogen bromide into bromine. This bromine, as in the previous case, reacts with the potassium iodide to give iodine, which is titrated with additional sodium thiosulfate. By subtracting twice this latter amount from the total bromine determined by the first titration, the true value of bromine addition is obtained.

There is no doubt but that this titration method is theoretically correct, so far as the chemistry of rubber is understood. The present authors have tried out this method in a sympathetic manner, with the full expectation that excellent results would be obtained. They have been somewhat disappointed in its workings although they believe that it will eventually be of good service.

DISCUSSION OF ERRORS

Substitution apparently always takes place. Hinrichsen[1] states that when the temperature is around 0° C., *only* the tetrabromide is formed, even though an excess of bromine is present. Our experience does not corroborate this. In a number of preparations of the tetrabromide from ordinary first latex pale crepe, as well as from specially purified rubber, we have always noticed that hydrogen bromide begins coming off after the first addition of the bromine solution. In these preparations the mixtures were well stirred and cooled approximately to 0° C. The amount of moisture in the solution or in the room was not enough to account for all the hydrogen bromide which came out of the solution. All the preparations, however, were made in diffused daylight, and the light, no doubt, had considerable effect on the reaction.

One theoretical possibility should be discussed here. Some of the hydrogen bromide formed in the substitution may add to a double bond. Such a reaction would prevent the regular addition of bromine. Since the amount of substitution is measured from the amount of hydrogen bromide and since free bromine cannot now add to the particular double bonds involved, it would seem that some error would certainly result. This, however, is not the case, as can be seen from the following considerations. The total bromine taken, less the excess of bromine as determined by titration, is equal to the amount of bromine actually used, A; the hydrogen bromide oxidized to bromine, the latter titrated and doubled, gives the amount of bromine used in substitution, B. A — B = the amount of bromine added to the double bonds. Now, if the reaction under discussion takes place, there will be a smaller amount of bromine used; in other words, A will be smaller; and, since some of the hydrogen bromide has added to the double bonds, this amount will not be oxidized and calculated as bromine substituted, which means that B will also be smaller, and by exactly the same amount of bromine as A. An equal amount will be subtracted from both A and B, and therefore the result will be the same as though the reaction had not taken place.

---

[1] The greater part of this paper was given in the Symposium on Analytical Chemistry before the Rubber Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920. The work on vulcanized samples has been completed since that time.

[2] Th. Budde, "The Valuation of Cold Vulcanized Rubber Ware by the Tetrabromide Method," *Apoth. Ztg.*, **24**, 529; *C. A.*, **3** (1909), 3013.

[3] THIS JOURNAL, **12** (1920), 673.

[4] *J. Am. Chem. Soc.*, **21** (1899), 1084.

[1] *Z. anorg. Chem.*, **81** (1913), 70; *C. A.*, **7** (1913), 2861.

One of the practical drawbacks of Lewis and McAdams' method is the fact that carbon tetrachloride is not a solvent for the rubber tetrabromide. The tetrabromide precipitates sometimes as a mushy mass consisting of fine white threads and sometimes as small white lumps. When the water solutions are added and the mixture shaken, an emulsion is often formed which is almost impossible to break. Similar emulsions, however, are formed even when such a solvent for the tetrabromide as chloroform is employed. The difficulty lies in the use of immiscible liquids. The precipitate in carbon tetrachloride occludes bromine, and this is only very slowly removed in the reaction during the titration. In testing out the method on pure rubber, the authors have found that better and quicker results can be obtained by adding an excess of the thiosulfate solution in the beginning of the titration and shaking vigorously in order to complete the reaction. A known excess of the bromine solution is then added, and the titration can be rapidly completed with more of the thiosulfate, since the bromine has not had any opportunity to be occluded by the precipitate. This procedure requires an extra calculation on account of the second addition of bromine, but it is much shorter and more accurate. The same method can be used in the titration following the addition of the iodate. In this instance the calculation must be watched, since the amount of bromine equivalent to hydrogen bromide is required. The amount of thiosulfate equivalent to the amount of bromine added in excess must be subtracted before the titration is doubled.

A blank determination under the same conditions is, of course, always run. In Lewis and McAdams' method there is an unfortunate error in the directions. The amount of potassium iodide is not enough to react with the bromine that is left unless a very heavy substitution has taken place. Even then much trouble will be met in running the blank if only 10 cc. of a 3 per cent potassium iodide solution are used, as directed. The molecular weight of potassium iodide is 165.9, almost twice the atomic weight of the bromine, 79.9, with which it reacts. If a 0.2-g. sample of pure rubber is used, 0.47 g. bromine is required theoretically, and the 150 per cent excess of bromine would amount to 0.71 g., a total of 1.18 g. bromine. This total amount would require 2.45 g. potassium iodide, whereas 10 cc. of 3 per cent potassium iodide contain only 0.3 g. potassium iodide. Therefore, even in the regular determination, it would be necessary to add more of the potassium iodide solution, and in the blank determination it is necessary to add considerably more, something like 90 cc., or, better yet, to use a smaller amount of a stronger solution (15 cc. of 20 per cent potassium iodide) in order to avoid the large amount of water.

It is absolutely necessary that an excess of potassium iodide be used, since bromine, like chlorine, reacts in a different way with thiosulfate than iodine. The equations for the bromine and iodine reactions are as follows:

$$Na_2S_2O_3 + 4\,Br_2 + 5\,H_2O \longrightarrow Na_2SO_4 + H_2SO_4 + 8\,HBr$$

$$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

In case some free bromine remains the first titration will of course be incorrect, as shown by the first equation, since bromine reacts with less thiosulfate. The hydrogen bromide that is formed at the same time will react with the potassium iodate and an entirely erroneous idea of the amount of bromine substituted will be obtained.

In our first blank experiments about 25 per cent more of the thiosulfate was required after the addition of the potassium iodate. The extra amount was not constant, since the amount of potassium iodide added was only approximately the same each time. After the proper amount of potassium iodide was used no further difficulty was experienced.

In the procedure for vulcanized rubber Lewis and McAdams use 10 cc. of 10 per cent potassium iodide, and it can readily be seen that this amount should be increased to something like 30 cc. for the blank.

PURE RUBBER SAMPLES

The results obtained with different samples of rubber were not always very concordant. In one instance an excellent check was obtained (0.15 per cent) but in another instance the difference amounted to 24.27 per cent. Even though a chloroform solution was used, the results were still several per cent off. The results of the present investigation are given in the following table:

RESULTS WITH PURE RUBBER[1]

EXPT. No.	Percentage Rubber Hydrocarbon CCl$_4$ Soln.	Percentage Rubber Hydrocarbon CHCl$_3$ Soln.	DIFFERENCE
A-1-A	99.89		
This was an unusually pure sample of rubber. It had been dissolved in pure benzene, precipitated in alcohol twice, extracted for 24 hrs. with acetone, redissolved, reprecipitated, and redissolved and kept in pure benzene. The sample for analysis was obtained by evaporating the benzene from some of the solution spread out on a warm glass plate. A good end-point was obtained and no color developed on standing.			
B-1-A	93.69		3.99
B-2-A	89.70		
First latex pale crepe extracted with acetone. Heavy emulsions were formed during the titrations and poor end-points were obtained.			
C-1-A	80.61		24.27
C-2-A	104.88		
Masticated first latex pale crepe, extracted with acetone. Heavy emulsions and poor end-points.			
C-1-B		73.09	4.31
C-2-B		77.40	
Same as C-1-A Emulsions formed. Long time to reach end-point. Large amount of HBr.			
E-1-A	98.56		0.15
E-2-A	98.71		
First latex pale crepe, dissolved in "90 per cent benzene" and precipitated three times with denatured alcohol. Samples kept between Holland cloth for several days. Heavy emulsions formed but they broke up easily. Good end-points.			
F-1-A	79.92		10.03
F-2-A	69.89		
Masticated first latex pale crepe dissolved in "90 per cent benzene" and precipitated in denatured alcohol four times Kept for several months under water. Poor end-points.			

[1] Only two sets of these determinations were made by using the excess of thiosulfate and further addition of bromine before the titration was completed. These are C-1-B and C-2-B, and E-1-A and E-2-A. In both E-1-A and E-2-A the excess was also added after the addition of the iodate solution and the best end-points and best check of all obtained.

VULCANIZED RUBBER SAMPLES

One of the difficulties encountered by the authors with vulcanized samples was that they could not always obtain complete solution in the tetrachloroethane, as recommended by Lewis and McAdams. Several types of rubber compounds were treated in the same way, that is, by extraction with acetone followed by treatment with alcoholic sodium hydroxide. (Lewis and McAdams give no data on the use of alcoholic potassium or sodium hydroxide, simply mentioning its use in a footnote for samples containing any vulcanized oil (factice).) Our samples were then dried on the steam bath. None of them, however, could be brought into solution even after 2 or 3 days of refluxing. It was considered that moisture was causing some of the trouble,[1] and since it was felt that in ordinary work it would not be advisable to use a vacuum dryer, a dehydrating agent, lime, was put into the solvent with the rubber. By this method 2-g. samples of a red inner tube were completely dissolved by refluxing for 12 hrs. A wire gauze was generally used in the heating, since tetrachloroethane boils at 147°, and scorching of the sample was often noted. The use of an oil bath, with the temperature of the oil kept not more than 20° above the boiling point of the solvent, did not prevent scorching. In one instance a sample containing reclaimed rubber was apparently completely dissolved after the long boiling; after standing, a portion was drawn off with a pipet and analyzed, but neither rubber nor sulfur was found in it—then it was noticed that the rubber had separated out as a jelly which was not taken up by the pipet. When the samples were not treated with alcoholic sodium hydroxide they dissolved in the tetrachloroethane within the specified time of 4 hrs.

As noted above, the amount of potassium iodide as given by Lewis and McAdams is not enough. About 30 cc. of 10 per cent potassium iodide should be used instead of 10 cc.

The authors have also used McIlhiney's first method[2] for determining the amount of substitution of bromine, which consists in titrating the hydrogen bromide formed as a by-product instead of oxidizing it with potassium iodate, and have obtained results which are comparable with those given by Lewis and McAdams. It does not seem, however, that the alkali titration offers any advantage over the iodate method. In a duplicate set of analyses of a red inner tube containing about 78 per cent of rubber hydrocarbon the results were as follows:

	A Per cent	B Per cent	DIFFERENCE Per cent
Rubber hydrocarbon, by bromination	78.30	71.44	6.86
Rubber hydrocarbon, equivalent of combined sulfur	5 68	5.31	0.37
Total rubber hydrocarbon	83.98	76.75	7.23

In the six different sets of analyses given by Lewis and McAdams the differences in individual runs for rubber hydrocarbon (by bromination) varied from 0.2 to 7.2.

THE COMPLETE METHOD

The complete procedure of Lewis and McAdams, together with our modifications and corrections, is briefly as follows:

Solvents and Solutions. *Acetone*—This should be freshly distilled over anhydrous potassium carbonate, the fraction coming over from 56° to 57° C. being used.

Carbon Tetrachloride—Purify by subjecting to the action of saturated chlorine water for several days in diffused daylight or by placing the mixture on a shaking machine for 6 hrs. during the day. Wash thoroughly with distilled water, dry over lime, and distil. Use a 1° fraction.

Bromine Solution—0.5 *N* solution in purified carbon tetrachloride.

Sodium Thiosulfate—0.25 *N* solution.

Potassium Iodide—20 per cent solution.

Potassium Iodate—5 per cent solution.

Starch—(soluble).

Tetrachloroethane—Purified in the same manner as the carbon tetrachloride. B p, 147° C.

Alcoholic Sodium or Potassium Hydroxide—1 *N* solution.

For Raw Rubber—Extract the weighed sample (not over 2.0 g.) in a standard extraction apparatus[3] with 60 cc. of acetone continuously for 8 hrs. Aspirate dry carbon dioxide through the extracted sample to remove the traces of acetone or transfer it on a watch glass to a desiccator and allow it to stand over concentrated sulfuric acid under reduced pressure. Dissolve the complete sample in about 250 cc. of purified carbon tetrachloride, with frequent shaking, slightly warming the solution on the steam bath if desired, in order to hasten solution. In the latter case be sure not to allow any moisture to get into the flask. Make up to exactly 500 cc. in a calibrated flask.

To a 50-cc. portion of the rubber solution in a 250-cc. glass-stoppered Erlenmeyer flask add from a buret 30 cc. of the standardized 0.5 *N* bromine solution (150 per cent excess of bromine above that necessary for addition —in this case the 30 cc. is calculated on 0.2 g. of rubber hydrocarbon), stopper tightly, carefully mix by gentle rotation, and set aside in a dark closet at the ordinary temperature for 2.5 to 3.5 hrs. Before removing the flask from the dark, cool by immersion for several minutes in ice water. Then, in a darkened room, attach a soft rubber tubing, 1 in. wide and 1.5 in. long, to the top of the flask and pour in 15 cc. of 20 per cent potassium iodide solution. Loosen the stopper and allow part of the solution to run in, shake gently, allow the remainder to run in, and wash with a stream of water. In this way no hydrogen bromide is lost. Still in the darkened room, titrate the free iodine that is formed with 0.25 *N* standard thiosulfate solution, using starch paste as an indicator. Rotate gently at first, add a slight excess of thiosulfate, stopper, and shake vigorously, add enough bromine solution to color the mixture, and complete the titration rapidly with more thiosulfate. In order to determine the amount of substitution, add 10 cc. of 5 per cent potassium iodate and titrate again with thiosulfate as above, adding an excess, etc. The total time of titration will take from 8 to 20 min., depending largely on how well the emulsion settles out. Violent shaking is necessary in order to remove the bromine which is occluded in the lumps of tetrabromide.

Run a blank determination at the same time in order to determine the bromine under similar conditions and to eliminate any error caused by impurities, etc.

Sample Calculation—Equivalent weight of rubber hydrocarbon $(C_{10}H_{16})n$ = 34. Thiosulfate solution = 0.230 *N*.

Sample of rubber	0.2078 gram	
Blank titration	61.06 cc.	thiosulfate
First titration (excess of bromine)	28 65 cc.	thiosulfate
Bromine consumed	32.41 cc	thiosulfate
Twice second titration (after proper subtraction of bromine used in excess)	6.22 cc.	thiosulfate
True addition	26.19 cc.	thiosulfate

$$\frac{26\ 19 \times 34 \times 0\ 230 \times 100}{0.2078 \times 1000} = 98.58 \text{ per cent}$$

For Vulcanized Rubber—Extract a weighed sample (approximately 1.5 to 2.0 g.) of vulcanized rubber with acetone for 8 hrs. in the standard extraction apparatus, evaporating the acetone to obtain the percentage of acetone-soluble material. Remove the acetone from the residue as indicated above, dissolve the complete sample[1] in 100 cc. of purified tetrachloroethane by refluxing for 4 hrs., cool, and make up to mark in a 250-cc. calibrated flask with purified carbon tetrachloride. Remove a 25-cc. aliquot portion by applying gentle suction to a pipet containing a small piece of cotton in its tip, deliver into a 250-cc. glass-stoppered Erlenmeyer flask, and proceed with the addition of bromine, as above. In this case only 100 per cent excess of bromine, calculated on the sample used, is necessary, since there is a smaller amount of the original rubber hydrocarbon present in the vulcanized material.

Determine the combined sulfur in the sample by evaporating an aliquot part of the tetrachloroethane solution and determining the sulfur in it.

Calculations for Vulcanized Rubber—The rubber hydrocarbon combined with the sulfur is found by multiplying the percentage of sulfur by $\frac{C_{10}H_{16}}{S_2}$ or $\frac{136}{64} = 2.13$. The total rubber hydrocarbon is then calculated by adding the percentage of rubber hydrocarbon combined with the sulfur and that of the uncombined rubber hydrocarbon found from the bromine addition.

The authors are very much indebted to Dr. W. W. Evans for his helpful suggestions and interest in this work.

SUMMARY

1—The precipitated tetrabromide occludes bromine which is only very slowly removed during the titration.

2—An improvement is suggested in the manner of titrating the bromine.

3—Emulsions are often formed during the titration which are sometimes very difficult to break. The heavier the emulsion, the greater the discrepancy in the results. The authors were unable to break the emulsions every time and are unable to tell how to avoid them. Chloroform, which is a good solvent for the tetrabromide, was tried, but although no precipitate came down, emulsions were formed.

---

[1] All the solvents were purified as described by Lewis and McAdams, and the moisture could not have come from them.

[2] *J. Soc. Chem. Ind.*, **13** (1894), 668.

[3] THIS JOURNAL, **9** (1917), 314. Use a hardened filter paper.

[1] In case "factice" (vulcanized oil) is present, the extracted sample should be boiled with 50 cc. of 1 *N* alcoholic sodium or potassium hydroxide for 2 to 4 hrs., filtered by decantation through a hardened filter paper, washed with alcohol, and dried over concentrated sulfuric acid under reduced pressure. The sample after this treatment will not dissolve readily in the tetrachloroethane, but can be brought into solution by adding some lime and heating for about 12 hrs. instead of 4 hrs.

4—Two errors in the original articles are pointed out, relative to the amount of potassium iodide used.

5—The results of several analyses of purified rubber are given, which show differences from 0.15 to 24.27 per cent.

6—If vulcanized samples are treated with alcoholic sodium hydroxide in addition to the acetone extraction, it is found that they do not dissolve in the tetrachloroethane within 3 days' heating. By adding lime to the solvent and rubber they can be dissolved in about 12 hrs.

7—Titration of the hydrogen bromide with alkali has no special advantages over the iodate method described in the original article.

8—The method requires further study and elaboration before it can be used with accuracy.

Reactions of Accelerators during Vulcanization. III—Carbo-Sulfhydryl Accelerators and the Action of Zinc Oxide[1]

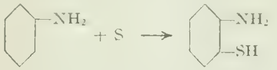
By C. W. Bedford and L. B. Sebrell

Goodyear Tire & Rubber Co., Akron, Ohio

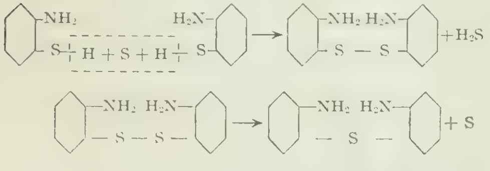
There seems to be a slowly but steadily increasing interest in the chemical reactions which organic accelerators undergo during the vulcanization of rubber. The chemistry of the sulfur reactions of organic nitrogen compounds has previously found its main application in the sulfur dye industry, and even after years of world-wide research it is still a desert, with here and there an oasis of definite knowledge regarding chemical composition or mechanism of reaction. Sulfur dyes are exhaustively sulfurated at high temperatures as compared with the use of the same or similar nitrogen compounds as accelerators in the vulcanization of rubber. Here we find a lower temperature and a lower quantity of sulfur as well as the use of shorter time, so that the chemistry of the first reactions of nitrogen compounds with sulfur may be applied to accelerators.

REACTIONS OF ANILINE WITH SULFUR

Merz and Weith[2] were the first to study the sulfuration of pure organic compounds. As early as 1869 they heated aniline with sulfur and studied the reaction products. According to Lange,[3] the first step in this reaction is the formation of a carbo-sulfhydryl group in ortho position to the amino group, giving *o*-aminothiophenol as the first intermediate product.



Further reaction with sulfur oxidizes two moles of the mercaptan to one mole of the disulfide, forming *o*-dithioaniline. At a higher temperature the disulfide loses one sulfur and changes to the monosulfide.

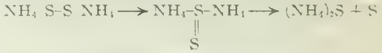


The above are typical equations which apply to practically all the reactions of sulfur with the benzene nucleus of accelerators, and while they may not take place with sufficient rapidity at curing temperatures to be considered as a part of the mechanism of vulcanization by aniline, they are instructive as a basis for comparison with the following sulfur reactions of other accelerators.

MECHANISM OF VULCANIZATION WITH AMMONIUM SULFIDE

Kratz, Flower and Shapiro[1] have found that ammonium hydrosulfide (NH_4SH) will vulcanize rubber without the use of free sulfur. They used a milled stock which, as is well known, is honeycombed with air bubbles, and heated it in a bomb tube containing ammonium hydrosulfide and air. The sulfur available for vulcanization comes from the atmospheric oxidation of the sulfhydryl groups to disulfides and the further decomposition of the disulfides to monosulfides and free sulfur or polysulfide sulfur, as in the above sulfur reactions of aniline. This is the same reaction which causes a colorless solution of ammonium sulfide to turn yellow or red on standing on the laboratory shelf in contact with air.

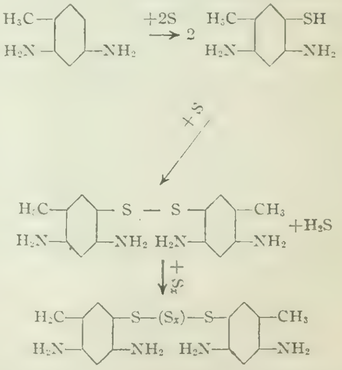
$$NH_4{-}SH + O + HS{-}NH_4 \longrightarrow NH_4{-}S{-}S{-}NH_4 + H_2O$$



$$NH_4{-}S{-}S{-}NH_4 \longrightarrow NH_4{-}\underset{\overset{\|}{S}}{S}{-}NH_4 \longrightarrow (NH_4)_2S + S$$

SULFUR ON *m*-DIAMINES

There are many dithio compounds, similar to the above dithioaniline, and containing the grouping $\equiv C{-}S{-}S{-}C\equiv$, which have been described, and we attach great importance to their property of picking up extra sulfur to form polythio compounds. Kalle[2] found that *m*-diamines react readily with sulfur, some at as low a temperature as 80° C. Schultz and Beyschlag[3] working with *m*-tolylenediamine, proved that carbo-sulfhydryl groups are first formed, which further oxidize to disulfides and that these disulfides have the power of forming polysulfides similar to ammonium polysulfide.



These investigators found this disulfide-polysulfide to be soluble in hydrochloric acid without loss of the polysulfide sulfur except after long standing. They also found this super-sulfur to be available for further sulfuration of amines or for further sulfuration in the nucleus of the disulfide itself.

---

[1] Presented before the Rubber Division at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *Ber.*, **2** (1869), 341; **3** (1870), 978; **4** (1871), 384.

[3] "Die Schwefelfarbstoffe," 18.

[1] THIS JOURNAL, **13** (1921), 67.

[2] D. R. P. 86,096.

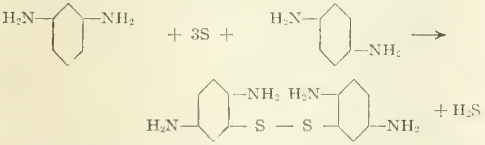
[3] *Ber.*, **42**, 743, 753.

The reactions of amines with sulfur frequently appear to be autocatalytic, the disulfides, once formed, producing polysulfide sulfur which is more active than the original elemental sulfur. In many cases and for the same reason, we are able to produce greater curing power or entirely different physical properties in a rubber stock by causing the accelerator to react with sulfur before compounding. This is especially true with accelerators which react slowly with sulfur or which lose none of their basic nitrogen during the sulfur reaction.

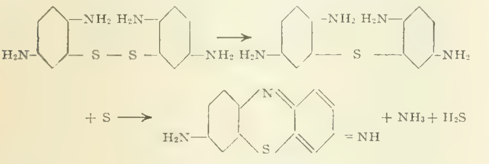
The curing power of *m*-tolylenediamine is evidently not due to the liberation of ammonia, as will later be shown to be the case with para-diamines. No ammonia is lost on heating this meta-diamine with sulfur up to 160° C., which is at least 18° C. above the curing temperature of 40 lbs. steam, while the reaction to form disulfide-polysulfides may be completed at 80° C. At temperatures of 180° to 200° C. ammonia is lost, as well as more hydrogen sulfide. The curing power of *m*-tolylenediamine or its disulfide is therefore attributed to the rapid formation of the disulfide-polysulfide without the loss of ammonia, and to the activity of this polysulfide sulfur as differentiated from any form of elemental sulfur.

Sulfur on *p*-Diamines

The meta position of the amino group seems to be necessary for the formation of stable disulfides and the retention of all the nitrogen. *p*-Phenylenediamine, when heated with sulfur at curing temperatures, liberates ammonia and hydrogen sulfide, forming thionine or Lauth's Violet.[1] In writing the equations for this reaction we first assume a mechanism similar to that of the meta-diamines.



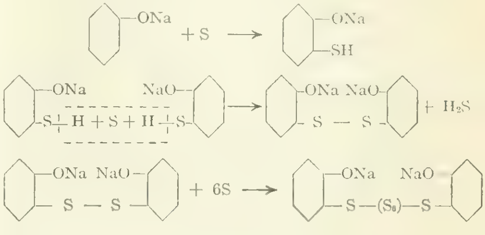
This para-diamine disulfide is evidently unstable at the temperature necessary for a sulfur reaction with the amine and breaks down by heat into the monosulfide, thereby bringing the two amino groups into such close proximity that one of the nitrogens is liberated as ammonia and further oxidation by sulfur gives the chromophore grouping.



This purple dye shows about the same curing power as the corresponding amount of aniline. The curing power of *p*-phenylenediamine, however, is so much greater than the corresponding amount of aniline or of the purple dye, especially in the curing of hard rubber, that we are forced to consider its action as due chiefly to the liberation of ammonia and hydrogen sulfide with the subsequent formation of ammonium polysulfide.[2]

Sulfur on Phenolates

The sodium phenolates used as accelerators by Porritt[1] have been considered simply as a means of obtaining a perfect distribution of caustic in a rubber mix. Molau and Seyde[2] and Haitinger,[3] however, have shown that at 100° to 115° C. there is an easy reaction with sulfur to form thiophenols, disulfides, and polysulfides in the same manner as with aniline or the meta-diamines.[4]



Here we have the complication of two or more possible mechanisms for the formation of polysulfide sulfur. The group $\equiv C-S-S-C\equiv$ easily forms polysulfides, the sodium atom may pass from the hydroxy group to the sulfhydryl group which is the stronger acid, and the sodium salt of the mercaptan may then form polysulfides or the sodium may be removed by hydrogen sulfide and form sodium polysulfides. Perhaps future research will decide whether one or all of these reactions function during vulcanization.

The presence of alkali materially lowers the temperature necessary for a rapid reaction of sulfur with phenol, as is the case with many of the compounds used in the manufacture of sulfur dyes. The inorganic polysulfides of sodium or potassium furnish active sulfur which will react with organic materials at temperatures lower than that required by elemental sulfur. Organic polysulfides seem to act in the same manner and the sulfuration of many organic compounds shows evidence of autocatalysis. It is this same principle which is responsible for the polysulfide theory in the vulcanization of rubber.

Lange[5] quotes Molau and Seyde and states that most of the sulfur dyes are considered as aromatic derivatives of hydrogen polysulfide. Very few of the sulfur dyes, however, are good accelerators after the removal of the alkali. The temperatures used in their manufacture are so high and the amounts of sulfur used are so large that sulfuration is evidently carried too far or the disulfides are changed to monosulfides, for it is our experience that the best of the mercapto or disulfide accelerators lose much of their curing power by overheating.

Sulfur on Aldehyde Ammonia

There are some investigators who do not look with favor on the theory that most accelerators enter into chemical reaction with sulfur before they activate the balance of the sulfur. Twiss and Brazier,[6] evidently discussing our British patent,[7] state that "this view may be correct in certain cases, but evidently cannot be accepted generally for all vulcanization catalysts." They refer to their work showing aldehyde ammonia to function as a powerful accelerator at as low a temperature as 98° C. and comment that "this observation militates against the belief of some investigators in this field that vulcanization catalysts are not themselves able to expedite vulcanization, but that during early stages of the process they combine with sulfur, giving rise to substances which possess the desired activity." We fail to follow their logic, especially in the case of aldehyde ammonia, which is one of the most striking examples of an accelerator which violently reacts with sulfur.

---

[1] Lange, "Die Schwefelfarbstoffe," 40.

[2] If *p*-phenylenediamine be heated with sulfur under reflux, the condenser tube frequently clogs up with the alkaline compounds of ammonia and hydrogen sulfide described in Watt's Dictionary, Vol. I, 204.

[1] Brit. Patent 129,798 (1919).

[2] *Chem.-Ztg.*, **1907**, 937; *Z. phys. Chem.*, **54**, 274.

[3] *Monatsh.*, **4**, 163.

[4] Lange, "Die Schwefelfarbstoffe," p. 96, gives several other important references.

[5] *Ibid.*, p. 97.

[6] *J. Soc. Chem. Ind.*, **39** (1920), 125*t*.

[7] Brit. Patent 130,857 (1919).

Using temperatures much lower than the 98° C. of Twiss and Brazier, we find that aldehyde ammonia reacts vigorously with sulfur in boiling alcohol with the loss of ammonia and hydrogen sulfide, giving a reddish brown resinous product of comparatively low curing power. By far the largest portion of the curing power of aldehyde ammonia is lost in the two gases which form ammonium polysulfide during vulcanization. A control test, made by boiling aldehyde ammonia in alcohol without sulfur, gave only a trace of ammonia and the solution was only slightly colored after 5 hrs.' boiling, the aldehyde ammonia being recovered almost unchanged. This accelerator affords another very good means of compounding ammonia and hydrogen sulfide, being similar in this respect to *p*-phenylenediamine.

Stevens[1] has pointed out that our theory of sulfur reaction of accelerators must necessarily include an efficiency factor depending upon the rate of reaction between accelerator and sulfur. In the British patent above mentioned it is stated that "the temperatures used in the vulcanization of caoutchouc are only occasionally and by the merest coincidence the temperatures most suitable for a reaction between sulfur and a nitrogen accelerator." It is certainly true that we unconsciously choose accelerators on this very factor and that we discard many accelerators as worthless, such as carbanilide after testing it at 40 lbs. steam pressure, whereas at 60 lbs. pressure it is a rapid accelerator. There are still other factors than temperature, such as the action of secondary or inorganic accelerators and the ratios of sulfur and accelerators to each other and to the rubber.

NITROSO ACCELERATORS

Stevens[2] also gives a very pertinent criticism of our theories regarding the action of nitroso accelerators. He states that since *p*-nitrosophenol is an accelerator and *p*-aminophenol is not, he cannot support the idea that nitroso accelerators first react with hydrogen sulfide to produce amido-accelerators. A recent Canadian patent[3] has announced the hydrogen sulfide reaction product of *p*-nitrosodimethylaniline as a vulcanization accelerator. A similar reaction takes place between *p*-nitrosophenol and hydrogen sulfide, but the reduction product is not an accelerator, on account of the acidic action of the hydroxy group. Nitrosophenol, nevertheless, is a strong oxidizing agent and will speed any organic reaction wherein hydrogen sulfide is formed by oxidizing and removing the same. An example of this action is the almost instantaneous formation of thiocarbanilide from carbon disulfide and aniline by the addition of nitroso compounds.[4]

We attribute the curing power of nitroso accelerators first to their oxidizing power, which will greatly speed the reaction of the sulfur with accelerator, rubber resin or rubber protein, thereby bringing the nitrogen in the rubber into quicker action as an accelerator. In this sense, therefore, nitroso accelerators are, first of all, secondary accelerators acting in the same manner as litharge. Nitrosophenol has this type of accelerating power and the fact that its reduction product is not a primary accelerator has no bearing on its action as a secondary accelerator.

In the latter portion of this paper it will be shown that a rubber-sulfur-zinc oxide cement will not air-cure or gel by the addition of *p*-nitrosophenol and carbon disulfide, but that if the nitrosophenol be first reduced with hydrogen sulfide the cement will gel or air-cure within a few hours. The acidic properties of *p*-aminophenol evidently prevent its action as a primary accelerator but do not prevent its reaction with carbon disulfide to form dithiocarbamates whose zinc salts will vulcanize a rubber cement at room temperature. It may also be noted that the corresponding thiourea, *p,p*-dihydroxydiphenylthiourea, is a fair accelerator for vulcanizing rubber.

EXPERIMENTAL PART

The carbo-sulfhydryl accelerators constitute the most important class of vulcanization aids known to-day. Thiocarbanilide is probably used in larger tonnage than the gross weight of all other accelerators put together. Other than thiourea derivatives, this class includes the thiurams, dithiocarbamates, mercaptans, mercaptides, disulfides and all accelerators which produce these or similar compounds during the vulcanization process. In considering the class as a whole, one cannot overlook the great effect that zinc oxide has on the curing power of these accelerators, and it soon becomes evident that the action of the secondary accelerator must be known before much can be done to explain the action of the primary accelerator. The dithiocarbamates and their ability to cure rubber compounds at ordinary temperatures, seemed to the authors to offer a suitable basis for research on the action of the metallic oxide and as a result the data in Table I were obtained.

The zinc oxide cement used in these experiments was prepared from a milled stock consisting of pale crepe 100.0, ZnO 10.0, and sulfur 6.0. This compound was made into a benzene cement and distributed in wide-mouth glass bottles, so that each bottle contained 118.0 g. cement, or 10.0 g. compound and 108.0 g. benzene. The weights given in Table I indicate the amounts of chemical added to each bottle. In many cases the weight of accelerator is equal to or greater than the entire weight of rubber per bottle. This was done in order to shorten the time required for the test, as well as to show up weak curing action that might otherwise be overlooked. The values for combined sulfur are calculated as parts per 100 parts rubber (S_c) and are qualitative only, since the ages of the different samples were not necessarily the same at the time of analysis.

In several of the bottles the zinc oxide entirely disappeared and the cement took on the appearance of a pure gum cement with none of the milkiness remaining, and on longer standing there appeared large concretionary crystals containing zinc, which the authors believe to be the zinc salt of the dithiocarbamate. This action is indicated in the right-hand column as "Clear" and "Cryst."[1]

A repetition of all of the above experiments in absence of zinc oxide gave negative results in every case with the exception of the three zinc salts, namely: zinc ethyl xanthate, zinc thiophenol, and zinc mercaptobenzothiazol. It is to be noted that two of these compounds are nitrogen-free and without basicity other than that due to the presence of the zinc. The xanthate and thiophenol were prepared without the use of nitrogen in any form and were washed free from caustic which even if present would not cause the cement to gel. All three of these accelerators, and the mercaptans of the last two, function in regular heat cures.

---

[1] *India Rubber J.*, **62** (1920), 719.

[2] *Loc. cit.*

[3] Bedford and Sibley, Can. Patent 207,982 (1921).

[4] Bedford and Sibley, Can. Patent 207,983 (1921).

[1] In many of the tests there also appeared a cloudy precipitate. A similar precipitate forms after a few hours on dissolving zinc thiophenol and sulfur in cold aniline or at once on heating. The composition of these precipitates have not yet been studied.

TABLE I—ZINC OXIDE CEMENT

CHEMICAL	Weight Grams	Cement Set	Time	S_c on R	Remarks Clear	Remarks Cryst.
Aniline	10.0	No	2 mo.			
+ H_2S		No	2 mo			
Aniline (2 mol.) + CS_2 (1 mol.)	2.0	Yes	14 days	1.05	13 days	13 days
	5.0	Yes	36 hrs	0.66	2 days	8 days
	6.6 (1/20 mol.)	Yes	24 hrs.	1.04	20 hrs	5 days
	10.0	Yes	20 hrs.			
Aniline (2 mol.) + CS_2 (2 mol.)	1.0	Yes	3 mo			
	2.5	Yes	8 days			
	5.0	Yes	14 hrs.	1.12	14 days	14 days[1]
	8.5 (1/10 mol.)	Yes	10 hrs.	0.53	8 days	10 days
o-Toluidine +	5.3	Yes	20 hrs.	1.04	6 days	None
CS_2 (1/20 mol.)	3.8					
m-Toluidine +	5.3	Yes	18 hrs.	1.06	48 hrs.	6 days
CS_2 (1/20 mol.)	3.8					
p-Toluidine +	5.3	Yes	3 days	0.88	22 hrs	6 days
CS_2 (1/20 mol.)	3.8					
Dimethylaniline	5.9	No	2 mo.			
+ CS_2	3.8					
p-Phenylenediamine	5.4	No	2 mo			
+ CS_2	3.8					
Thiocarbanilide	11.4	No	2 mo			
+ NaOH		No	2 mo.			
+ CS_2		No	2 mo.			
+ PbO	4.7	No	2 mo			
+ $C_6H_5NH_2$	4.7	Yes	10 days			
p-Nitrosodimethyl-Aniline	6.8	No	2 mo.	Cement becomes thinly liquid		
+ CS_2		No	2 mo.			
+ H_2S		No	2 mo.			
+ H_2S + CS_2		Yes	5 days			
p-Nitrosophenol	6.2	No	2 mo.			
+ CS_2		No	2 mo.			
+ H_2S		No	2 mo			
+ H_2S + CS_2		Yes	6 days			
Ammonia gas		No[2]	2 mo.			
+ H_2S		No[2]	2 mo.			
+ CS_2		No[2]	2 mo.			
+ H_2S + CS_2		No[2]	2 mo.			
Ammonium polysulfide, aq.		No[2]	2 mo.			
Sodium sulfide, aq.		No[2]	2 mo.			
Caustic soda, aq.		No[2]	2 mo.			
Sodium ethyl xanthate		Yes	16 days 30 days		Thin gel Thick gel	
Zinc ethyl xanthate		Yes	24 hrs.			
Thiophenol	5.5	No	2 mo.	Zn salt does not form		
Zinc thiophenol	7.1	Yes	48 hrs.			
Piperidine	3.0	No	2 mo.			
+ H_2S		No	2 mo.			
+ thiophenol		No[3]	2 mo.			
+ CS_2		Yes	24 hrs. or less			
Mercaptobenzothiazol		Yes	7 days or less	Zn salt forms slowly		
Zinc mercaptobenzothiazol		Yes	48 hrs.			

[1] Large crystals dispersed in perfectly clear cement.

[2] Alkali, whenever used, causes a thickening of the cement, due to the effect of the alkali on the rubber. This is noticeable at once for NaOH, and after a few days for NH_4OH.

[3] The cement thickened at once owing to the mass of crystals of the piperidine-thiophenol salt, but quickly thinned out with more benzene

ZINC MERCAPTIDES In a number of cases, such as with the toluidines, the acetone extract of the solvent-free, air-cured vulcanizate was found to contain large amounts of zinc in solution as shown by zinc oxide in the ash. This fact, together with the disappearance of the zinc oxide in the cements, indicated a soluble zinc compound, probably the zinc salt of the dithiocarbamate. On the same basis, the action of thiocarbanilide of air curing in the presence of aniline and zinc oxide was supposed to function through the zinc salt of the tautomeric or mercapto form of the thiourea. The following tests tend to corroborate this assumption.

Several of the cement tests were repeated, leaving out the rubber and sulfur. The soluble zinc was decermined by filtering, evaporating the solvent, and ashing the residue. The solutions, after filtering, were exposed to a beam of light in a dark room and found to be as free from colloidal particles as could be expected in solutions prepared in the open laboratory. These tests were confined to the thioureas.

1—*Thiocarbanilide (1 mole) + Aniline (1 mole or excess). Dissolved in acetone or benzene*—On standing, large lemon-yellow crysatls are formed, often weighing nearly 2 g. Several years ago these crystals were analyzed (unpublished data by W. Scott) and found to consist of exactly one mole each of aniline and thiocarbanilide. The same crystals are obtained on crystallizing thiocarbanilide from aniline. We have previously mentioned the crystailine product formed by mixing one mole each of the two liquids, piperidine and thiophenol, which we believe to be salt of an organic acid and base and to contain pentavalent nitrogen as in ammonium sulfide. In the aniline-thiocarbanilide crystals here described, we believe the thiocarbanilide to be in the mercapto form and the crystals to be the aniline salt of the mercaptan. The crystals are stable only in contact with the mother liquors, and easily decrepitate into aniline and flat crystals of thiocarbanilide. The best proof of the mercapto form of thiocarbanilide in contact with aniline is its extraordinary reactivity in dissolving zinc oxide, which power it does not have in absence of a basic amine.

2—*Thiocarbanilide and Zinc Oxide in Benzene*—No zinc oxide was dissolved, as indicated by filtering, evaporating, and ashing.

3—*Aniline and Zinc Oxide in Benzene*—No zinc soluble.

4—*Thiocarbanilide, Aniline, and Zinc Oxide in Benzene*—On standing at room temperature with frequent shaking for 18 to 24 hrs., large amounts of zinc are found in the clear filtered solution.

5—The above tests were repeated with zinc hydrate with the same results. The amount of zinc dissolved in Test 4 was higher than for the oxide.

6—In a few cases the residual zinc oxide, as filtered off and washed, was found to contain small amounts of sulfide, but usually there was no test for hydrogen sulfide on treating with acid.

7—To date, the organic zinc compound which is soluble in benzene, acetone, or aniline has not been isolated or its properties determined. Assuming that it is the zinc salt of the carbosulfhydryl form of thiocarbanilide (R–S–Zn–S–R) the following quantitative data were calculated to the percentage of the thiourea transformed to its zinc salt.

TABLE II

	Grams
Thiocarbanilide	22.8 (1/10 mole)
Aniline	93.0 excess
Zinc oxide	10.0 excess
Benzene	200.0
Total	325.8
Total organic	315.8

TIME Hrs.	Temp. °C.	Total Zn in Soln. (as ZnO) Gram	Thiourea Transformed to Zinc Salt	
			Weight Gram	Per cent
16	Room	0.04	0.225	0.99
40	Room	0.09	0.507	2.22
84	Room	0.16	0.903	3.95
Di-*o*-tolylthiourea 25.6 g. *o*-Toluidine 107.0 g. ZnO 10.0 g. Benzene 200.0 g.				
16	Room	0.075	0.474	1.85
40	Room	0.160	1.013	3.95
84	Room	0.211	1.340	5.23
(Same as above without the benzene)				
45 min.	100	0.242	1.510	5.9
105 min.	100	0.324	2.045	8.0
105 min. 24	100 Room	0.383	2.425	9.5
Di-*o*-tolylthiourea 64.0 g. *o*-Toluidine 321.0 g. ZnO 10.0 g.				
16	100	0.723	4.70	7.3
64	100	1.391	9.05	14.2

We find, therefore, an exact parallel between the solubility of zinc oxide in a benzene solution of thiocarbanilide and the air-curing of a similar rubber-sulfur-zinc oxide cement. Thiocarbanilide or aniline alone will neither vulcanize the cement nor dissolve the zinc oxide, while the combination of the two causes both reactions to take place.

The action of zinc oxide as an activator for thiocarbanilide and a retarder for aniline have been the subject of much recent discussion. It now appears that the first mechanism of its action with carbo-sulfhydryl accelerators is to form a zinc salt or mercaptide of the general formula R–S–Zn–S–R, which in some manner is able to activate the sulfur and hand it on to the rubber. By preparing these mercaptides before compounding the zinc may be used in much lower quantities and pure gum cements may be made to cure at ordinary temperatures.

SUMMARY

1—The vulcanization of rubber by ammonium hydrosulfide has been explained by oxidation and the liberation of free sulfur from the disulfide. The loss of S_x from polysulfides has previously been proposed as the mechanism for vulcanization.

2—Meta-diamines are differentiated from para-diamines by their sulfur reactions. *m*-Tolylene-diamine forms stable disulfide-polysulfides to which its curing power is attributed.

3—Sodium phenolates form disulfide-polysulfides similar to the meta-diamines and aniline.

4—Aldehyde ammonia is very rapid in its reaction with sulfur at or below curing temperatures, and forms ammonium polysulfide during vulcanization.

5—*p*-Nitrosophenol is believed to function only as a secondary accelerator, acting in this manner similarly to litharge.

6—Zinc oxide or zinc mercaptides have been found necessary in all rubber cements which cure at room temperature.

7—Weak bases, such as aniline, will vulcanize a zinc oxide-carbon disulfide cement at room temperature, just as piperidine or dimethylamine.

8—In cements containing amine and carbon disulfide, zinc oxide is dissolved and the cement may take on the appearance of a pure gum cement.

9—A mixture of aniline and thiocarbanilide will dissolve zinc oxide at ordinary temperatures.

10—A mixture of aniline and thiocarbanilide will vulcanize a cement containing zinc oxide at room temperature, while either alone will not.

11—Zinc thiophenol and zinc ethylxanthate are given as two accelerators which are free from nitrogen or alkali and which function either in heat cures or in curing pure gum cements at room temperature. Zinc mercapto-benzothiazole acts similarly.

12—The ultimate mechanism of vulcanization by mercaptides and sulfur has not been discussed.

The Preparation and Instability of Tricalcium Arsenate[1]

By J. H. Reedy and I. L. Haag

Department of Chemistry, University of Illinois, Urbana, Illinois

Of late attention has been sharply directed to the instability of tricalcium arsenate, which is extensively used as an insecticide for certain crops. During storage this product undergoes some change in composition which results in a considerable increase in the amount of water-soluble arsenate. The latter substance is considered responsible for the "burning" of the foliage of the plants to which it is applied. At the time of preparation, according to the manufacturer's analysis, the soluble arsenate content is well within the limit (0.75 per cent As_2O_5), but upon reaching the consumer the value may be considerably in excess of this. Contact with moisture and carbon dioxide of the air was thought at first to be the cause of this deterioration, but the use of airtight containers has not been sufficient to prevent it. Furthermore, manufacturers have not been able to control their processes so as to give products of uniform composition. The material from one run may be thoroughly satisfactory, and that from the next may have to be rejected on account of excess of water-soluble arsenate.

EXPERIMENTAL

PREPARATION OF SALTS FOR CONTROLS—Three well-defined arsenates of calcium[2] are known: the normal or tricalcium arsenate, $Ca_3(AsO_4)_2$; the secondary or calcium hydrogen arsenate, $CaHAsO_4$; and the primary or monocalcium arsenate, $Ca(H_2AsO_4)_2$. The last of these is decidedly unstable, and its presence in the commercial product is unlikely.

Samples of the normal and secondary salts were prepared by the methods of Robinson.[3] For the former, calcium chloride and disodium arsenate were allowed to react in slightly acid solution. The latter was made by the action of arsenic acid solution on an excess of saturated calcium hydroxide solution. The precipitates were washed, dried, and analyzed, indicating the respective formulas, $CaHAsO_4.H_2O$ and $Ca_3(AsO_4)_2.3H_2O$. Robinson determined the solubility of these salts in 100 g. of water at 25° as: $CaHAsO_4$, 0.3308 g.; $Ca_3(AsO_4)_2$, 0.014 g. These pure salts were used as controls in the study of the products obtained by methods available for large-scale production.

INDUSTRIAL PREPARATION METHODS—While several methods suggest themselves for the manufacture of tricalcium arsenate, only one has been found in practice to give a satisfactory product at a sufficiently low cost. This involves the action of arsenic acid on a paste of slaked lime:[1]

$$3\ Ca(OH)_2 + 2\ H_3AsO_4 \longrightarrow Ca_3(AsO_4)_2 + 3\ H_2O \quad (1)$$

In the present work, a high-grade lime was slaked with three or four times its weight of boiling water, and a solution of arsenic acid was slowly added, with constant stirring, until the mixture was only faintly alkaline to phenolphthalein. This process involves approximately equal parts of lime and arsenic acid (estimated as As_2O_5), in the molecular proportion of 4 $CaO:As_2O_5$. The final product was assumed to be the tricalcium arsenate with an excess of calcium hydroxide.

The reaction between calcium chloride and trisodium arsenate gave a product that was unsatisfactory on account of the high water-soluble arsenate content. A batch of the material was made as follows: A solution of disodium arsenate was converted into the trisodium salt by adding a molecular amount of sodium hydroxide, and this was added to an excess of calcium chloride solution:

$$2\ Na_2HAsO_4 + 2\ NaOH + 3\ CaCl_2 \longrightarrow Ca_3(AsO_4)_2 + 6\ NaCl + 2\ H_2O \quad (2)$$

The by-product of Reaction 1 is water only, while the mother liquor of Reaction 2 contains sodium chloride and the excess of calcium chloride. These were removed from the precipitate by washing. However, the washings contained soluble arsenates, and the residue still remained high in soluble arsenates. The part played by these soluble salts in increasing the soluble arsenate content will be discussed later.

---

[1] Received June 13, 1921.

[2] Abegg, "Handbuch der Anorganischen Chemie," III (1907), 541.

[3] Oregon Agricultural Experiment Station, *Bulletin* **131** (1918).

[1] Cf. Haywood and Smith, U. S. Department of Agriculture, *Bulletin* **750** (1918).

It was concluded, therefore, that the lime paste-arsenic acid method is the most suitable process for preparing a satisfactory grade of tricalcium arsenate.

Further study has convinced the authors, on the other hand, that the whole technique of the preparation of tricalcium arsenate by the lime method is very important and most difficult to bring under control. The difficulties of the manufacturer in obtaining yields of low arsenate solubility have persistently appeared in this work. Hence attention was particularly directed toward the study of various influences that might affect the nature of the product.

TEMPERATURE EFFECTS—Without doubt, one very important influence is temperature, and here the results are somewhat conflicting with those of others, especially Haywood and Smith.[1]

Four samples of tricalcium arsenate were prepared by adding arsenic acid solution to calcium hydroxide solution (not the paste) until the mixture was only slightly alkaline. (Table I.) In the first two cases the calcium hydroxide was hot and the precipitate was washed with hot water; in the third and fourth cases the operations were at room temperature. The lime paste was used in the preparation of Samples 5 and 6. While the results for corresponding temperatures do not check very well, they indicate that, under the conditions employed, high temperatures favor low soluble arsenate values. It might be added that the experience of the manufacturers has led them to adopt the mixing of the solutions hot as the best plant practice. It is likely that the explanation of this temperature effect is that at low temperatures the speed of reaction is slow, so that the calcium hydrogen arsenate (probably formed as an intermediate product) is never quantitatively changed over into tricalcium arsenate, but is more or less occluded in the excess of the latter.

TABLE I—EFFECT OF TEMPERATURE ON WATER-SOLUBLE As_2O_5

SAMPLE	Temperature of $Ca(OH)_2$ ° C.	Total As_2O_5 Per cent	Water-Soluble As_2O_5 Per cent
1	80	42.88	1.53
2	80	41.92	2.43
3	23	40.78	8.41
4	23	41.32	9.25
5	80	43.70	0.28
6	23	43.70	1.62

ARSENIC ACID SOLUTION—The purity of the arsenic acid solution is of prime importance. The presence of nitric acid always resulted in high solubility, notwithstanding the fact that there was an ample excess of lime to effect its neutralization. Consequently it was found necessary to evaporate the arsenic acid solution, which was formed by the action of nitric acid on arsenic trioxide, on a steam bath as long as acid fumes were evolved.

LIME PASTE—Previous writers have pointed out that the lime used should be of high purity, and that it should be slaked to form a smooth paste. The presence of a considerable amount of calcium carbonate is objectionable in that it will not react with calcium hydrogen arsenate, and may therefore be responsible for the presence of this soluble material.

MIXING—Thorough mixing is also essential. The arsenic acid should be added slowly, so slowly that the mixture should at all times be alkaline. This is necessary to prevent the formation of acid arsenates, which seem to revert to the normal salt only slowly. Whether or not in the precipitation from hot solutions the stirring should be stopped just as soon as the acid solution has been added is hard to say. This point was investigated in the present work, and results seem to indicate that cooling without agitation gives the best product. The highest purity was obtained in runs that were allowed to stand over night before filtering.

Precipitation from hot solutions with vigorous stirring always resulted in a very fine precipitate, which upon drying gave a very friable, fluffy powder. Such a condition is necessary to insure a sufficient suspensibility to make the product serviceable as a spray material.

EXPOSURE TO AIR—Tricalcium arsenate deteriorates to a marked degree when exposed to air for a considerable length of time. Tables II and III show the effects of laboratory air and moist carbon dioxide, respectively. Confessedly, the latter is not comparable to ordinary air, but it does show in an exaggerated degree the change that takes place under atmospheric influence. The apparent capriciousness of the results may be due to the various degrees of impurity of the samples used. For example, Sample I may have had a higher content of free calcium hydroxide, which protected it to a large degree. However, the figures suggest that other influences than the removal of the free base are involved.

TABLE II—EFFECT OF EXPOSURE TO AIR OF LABORATORY

SAMPLE	Water-Soluble As_2O_5 Initial Value Per cent	After 4 Wks.' Exposure Per cent
C	0.35	3.69
I	0.07	0.52

TABLE III—EFFECT OF CARBON DIOXIDE

SAMPLE	Gain in Weight Per cent	Water-Soluble As_2O_5 Initial Value Per cent	After 24 Hrs.' Exposure Per cent
C	0.015	0.35	9.50
G	0.021	1.62	12.70
I	0.032	0.07	3.32

IMPURITIES—Table IV shows the effects of certain common contaminating substances, as compared with distilled water.

TABLE IV—EFFECT OF IMPURITIES IN WATER

SAMPLE	Amount of Water-Soluble As_2O_5 Distilled Water Per cent	Tap Water Per cent	0.02 Per cent NaCl Per cent	0.02 Per cent $FeSO_4$ Per cent
I	0.07	2.31	1.27	8.25
C	0.35	7.42	3.55	18.00
G	1.62	..	5.26	25.00

The tap water contained sodium, magnesium, and iron in the form of bicarbonates and sulfates, anions that are believed to be very active in the decomposition of tricalcium arsenate. The action of the nitric acid in the arsenic acid in causing high solubility, as mentioned above, falls under this head. In this case, it is the calcium nitrate that effects the decomposition of the material.

An excess of calcium hydroxide, on the contrary, has been shown by Robinson[1] to stabilize the product, reducing the amount of water-soluble arsenate to practically zero.

The various influences affecting the amount of soluble arsenate, as brought out in this work, are summarized in Table V. The property of suspensibility is relative, and was estimated by the volume of the precipitate and its slowness in settling. It will be noticed that the samples reported are, for the most part, high-grade products.

TABLE V—SUMMARY OF THE INFLUENCES AFFECTING THE QUALITY OF THE TRICALCIUM ARSENATE

SAMPLE	Temperature of Reaction ° C.	STIRRING	Acid Added	Stood before Filtering Hrs.	Water-Soluble As_2O_5 Per cent	SUSPENSIBILITY
A	80	Thorough	Slowly	0.5	0.23	Excellent
B	80	Thorough	Slowly	0.5	0.16	Excellent
C	80	Thorough	Slowly	0.5	0.35	Fair
D	80	Little	Fast	0.5	1.04	Poor
G	23	Thorough	Slowly	0.5	1.62	Poor
I	80	Thorough	Slowly	12	0.07	Good
J	80	Thorough	Slowly	12	0.09	Good

NATURE OF THE DECOMPOSITION

The reaction which occurs during the deterioration of tricalcium arsenate is evidently hydrolysis, and is represented by the following equation:

$$Ca_3(AsO_4)_2 + 2\ H_2O \rightleftharpoons 2\ CaHAsO_4 + Ca(OH)_2$$

Evidence to substantiate this assertion cannot be found in analytical data, since, until either calcium hydroxide or calcium hydrogen arsenate begins to precipitate, the composition of the dissolved substance will be identical with that of the solid. Very conclusive evidence, however, was brought out by the following experiment: Some tricalcium arsenate of the best purity was placed in a glass-stoppered bottle, covered with distilled water containing a few drops of phenolphthalein, and shaken occasionally for several days. A considerable alkalinity developed. To meet the objection that the alkalinity might be due to calcium hydroxide present in the arsenate, this water was drawn off, and analysis showed that it contained a corresponding amount of soluble arsenate. The water over a slightly impure sample (containing a trace of sodium chloride) reddened more rapidly than in the case of the pure substance.

---

[1] *Loc. cit.*

[1] *Loc. cit.*

This concept of a reversible hydrolysis also explains the other facts in the behavior of tricalcium arsenate. The stabilizing effect of the excess of lime is due to the repression of the hydrolysis. On the other hand, decomposition will be favored by introducing anything that will combine with the calcium hydroxide formed, such as acidic substances or materials that will convert it into a more insoluble compound. This is illustrated in the action of the tap water and of the ferrous sulfate (Table IV). The effect of the sodium chloride and calcium nitrate is probably of a different nature. The easiest and most direct explanation of such action is that the decomposition of tricalcium arsenate is catalyzed by the presence of soluble salts, a behavior exactly analogous to the action of salts in catalyzing the hydrolysis of esters.

This explanation, of course, is at variance with the assumption that tricalcium arsenate, since it is the most insoluble, is therefore the most stable of the calcium arsenates. Insolubility is not an infallible index of stability, as might be shown by citing a number of cases in which insoluble substances are hydrolytically converted into more soluble ones. Magnesium ammonium phosphate is a single example. From this point of view, tricalcium arsenate in contact with moisture is a metastable substance, and its transformation into the more stable secondary arsenate may be easily effected by many substances.

SUMMARY

1—The most favorable conditions for making a stable form of tricalcium arsenate that will have a low soluble arsenate content and be otherwise suitable for use as an insecticide on plants are: (*a*) high temperatures, (*b*) purity of materials, (*c*) excess of lime, (*d*) thorough mixing.

2—The water used in preparing sprays should be as pure as possible.

3—The decomposition of tricalcium arsenate is due to hydrolysis, which seems to be catalyzed by many substances that may be present as impurities.

Preparation of Mannose from Ivory-Nut Shavings[1]

By Paul M. Horton

Audubon Sugar School, Louisiana State University, Baton Rouge, Louisiana

For a number of years it has been customary in the chemical laboratory of the Louisiana State University to assign to advanced students in the Audubon Sugar School the preparation of various rare sugars in the pure form. These preparations as a rule were not very satisfactory, either as to yield or product, nor was it always easy to tell where the trouble lay. During the past few years the rare sugars, however, have been attaining considerable technical importance. The following description of the preparation of mannose presents our experience in an attempt toward its simplification. The procedure described has been tried out by six or eight students of average technique in organic chemistry with uniformly satisfactory results, both as to yield and quality. This procedure is presented not as offering anything essentially new, but in order that any one attempting to prepare this rather costly sugar may be assured of results.

Though mannose occurs in many substances, the usual source is ivory-nut shavings, a by-product in the manufacture of buttons. A review of the literature will indicate that the source of the mannose produced from this source is largely the reserve mannocellulose. Whether the nuts actually contain fructo-mannan or not is immaterial, but it is certain that gums and other extractives are present, complicating the procedure by the steps needed for their removal. By the older processes the final sirup was always difficult to crystallize, owing to the various impurities passing through. For this reason the mannose was usually first separated as the hydrozone.

Bourquelot and Herissey[2] probably first described the method of hydrolyzing mannocellulose by means of cold 75 per cent sulfuric acid, but C. S. Hudson[3] has recently much improved the procedure by crystallizing the sugar direct from glacial acetic acid, thus avoiding the use of the expensive reagent, phenylhydrazine acetate.

The method finally adopted in our laboratory is as follows:

Dissolve 20 g. of commercial sodium hydroxide in 2000 cc. of tap water and heat to boiling, preferably in a porcelain dish. Stir 175 g. of 20-mesh ivory-nut powder or shavings into the boiling solution and remove at once from the source of heat. Allow the mixture to stand for 1 hr. with frequent stirring. Filter off the deep brown extract, and wash the residue until the runnings are clear and neutral. This filtration can be carried out effectively in an 8-in. Büchner funnel with suction, using heavy toweling as the filtering medium. The residue is sucked dry and finally transferred to a tray and dried at room temperature or in an electric oven at not over 60° C.

Mix 130 g. of the absolutely dry residue with 130 g. of cold 75 per cent sulfuric acid (1000 g. of 1.84 acid plus 400 cc. water for stock). If the residue has been well dried there will be very little evolution of heat, and the absence of irritating vapors is especially noticeable as contracted with the results obtained when using the unextracted shavings. The heavy, brownish, dough-like mass may be allowed to stand indefinitely without much decomposition, although 6 hrs. are sufficient for the reaction. Dissolve the mass in water to obtain a final volume of about 1.5 liters. Heat to boiling and allow to simmer for at least 6 to 8 hrs., keeping the volume constant by adding water from time to time to replace evaporation. A reflux may be used.

At the end of this period there will still remain a brownish residue in the solution, consisting for the most part of the outer skin of the nuts, which will weigh not over 10 g. when dry. Without filtering, allow the solution to cool to room temperature. Prepare a creamy solution of calcium hydroxide by slaking 50 g. of freshly burned lime in about 300 cc. of warm water. When cold add to the mannose solution with violent stirring and agitation in order that no portion of the liquid may become alkaline, even temporarily. Filter combined precipitate of calcium sulfate and dissolved nut residue on cloth, without warming. The cake will be found very porous and easily washed. Heat the filtrate, which should be still faintly acid, to about 90° C. and add 10 g. of Norit or some other decolorant char. Cool, add an excess of pure precipitated chalk or barium carbonate, and again filter on cloth. The precipitate, consisting of the excess carbonate and char along the sulfate, will wash easily. The filtrate should be perfectly clear and must not change the color of either red or blue litmus.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *Compt. rend.*, **133** (1901), 302.

[3] *J. Am. Chem. Soc.*, **39** (1917), 170.

Evaporate under vacuum to a light sirup (150 to 200 cc.). Considerable inorganic matter (mostly calcium sulfate will crystallize out at this point. Pour the cloudy sirup into an equal volume of 95 per cent ethyl alcohol, heat to about 90° C., add 3 g. of Norit, and filter hot. Wash with 70 per cent alcohol, which neither precipitates sugars nor dissolves inorganic salts. This liquor will be almost water-white.

Again evaporate under high vacuum to an almost solid mass (96 per cent solids by refractometer), the last portion of the water being expelled with the water bath at about 85° to 90°. This is necessary to prevent overheating of the sirup, which will give a yellow color to the mass. When the water is practically all evaporated the sirup will commence to boil as a whole and will become a mass of bubbles. If it is removed from the source of heat, the sirup will collapse to the bottom of the flask in strings. The mass will flow only slowly if the boiling vessel is inverted. This amount of detail is given as it is important that the boiling be carried to the right point, and a refractometer is not always available.

Finally add an equal volume of warm glacial acetic acid and dissolve by warming and shaking. The sugar will go into solution rather slowly and in some cases it may be necessary to add 1 or 2 cc. of water as a last resort. Pour into a covered crystallizing dish and allow to stand for 24 hrs. before seeding. The sirup will crystallize within 3 days without seeding if the preparation is carried out carefully. Add small portions of acid (totaling 50 cc.) as crystallization proceeds.

If after 2 days no crystallization occurs, place the dish in a freezing mixture and freeze solid, stirring as long as possible. After thawing, out crystals will probably appear at once. As a last resort in obstinate cases, dilute with 400 cc. of water and reboil to a heavier sirup. In any event the acetic acid solution should be practically colorless.

Filter the mannose crystals on paper with suction, washing in succession with glacial acetic acid, alcohol and acid, pure alcohol, alcohol and ether, and finally with pure ether. The crystals may now be transferred to a mortar and ground with ether and refiltered.

The sugar is pure white and needs no further purification for ordinary purposes. Dry at 40° C. until absolutely fluffy and free from odor. The yield is about 40 g. The sugar has a sweet taste, followed by a bitter aftertaste.

It will be noticed that this method eliminates the use of lead subacetate and treatment with hydrogen sulfide, avoiding several difficult filtrations. Furthermore, it will be observed that the sirup will not assume a gelatinous consistency upon boiling down, thus indicating that gums and extractives are absent.

Comparison of Results in Desugarization with the Steffen Lime, Barium, and Strontium Processes[1]

By **Mich. Potvliet**

Dominion Sugar Co., Chatham, Ontario, Canada

As the scarcity of granulated sugar has made it possible to make large profits in the desugarization of beet molasses by means of the Steffen lime process, the latter procedure has shown very few improvements in its practical execution during the past years. The only improvement of importance consists in the possibility of grinding the burned lime to such a fineness as to permit a more easy and complete formation of saccharate and a greater saving of lime. A second improvement in the Steffen process has been the saving of the waste water or mother liquor. The war made it necessary to use every possible substitute for the potash which had been imported from Germany, and in some factories the waste waters from the Steffen house were evaporated, after the excess of lime compounds had been removed, for the purpose of recovering the potash. The process of concentrating this very dilute waste water was expensive and, owing to trouble with lime compounds, it was practiced in only a few factories. As soon as the market for potash is reëstablished, we may assume that the Steffen waste water will flow into the sewer as in former days.

About fifteen years ago an Italian chemist, Battistoni, used the barium oxide which he obtained in electric furnaces for the formation of barium saccharate. The juices from this saccharate apparently had many advantages over those of the Steffen lime process.

The strontium bisaccharate has lately attracted attention. This process has been used for many years in several factories in Germany, among which the factory at Dessau is the most important. The juices from this process also show marked advantages over the lime method. The writer proposes to compare these three processes of desaccharification.

If barium oxide and strontium oxide can be made more cheaply than at present, there is no doubt in the writer's mind that the Steffen lime process in the near future will be doomed.

EXPERIMENTAL

In order to compare the three methods, a molasses was worked with which had the following constant composition in all experiments:

Brix	84.5	Raffinose on 100 polarization	2.35
Polarization	51.1	Apparent purity	60.50
Sugar	48.5	Real purity	57.40
Raffinose	1.2		

In the discussion that follows, polarization always means the direct polarization, and sugar represents the real sugar after deducting raffinose. Furthermore, the final results of this paper are all based upon real sugar.

The lime used in the lime process was obtained by burning limestone in the ordinary vertical limekilns and was usually of a high grade. The barium oxide, used for making the solution of hydroxide, was obtained by the reduction of barium carbonate. The most complete reduction is obtained in an electric furnace, where the constant temperature and exclusion of gases from the oxide permit a yield of oxide as high as 95 per cent. The strontium oxide was obtained by reducing moist strontium carbonate, mixed with sawdust or powdered oil-cake, in a so-called cement kiln, which is a horizontal rotary kiln using fuel oil as a source of heat.

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

METHODS—In the lime process the very finely powdered lime was mixed in special "coolers" with the molasses diluted to 12° Brix, using small quantities of lime at a time and keeping the temperature around 10° C. The amount of lime used was usually about 110 per cent of the polarization. The saccharate which was formed was filtered off and washed with lime water.

In the barium process the undiluted molasses was mixed with a hot concentrated solution of barium hydroxide of 76° Bé. at 85° C. and the mixture was kept at 65° C. The saccharate formed within a few minutes and was collected in special, conical, low cylinders with screen bottoms and was washed with a 2 per cent barium hydroxide solution. The amount of barium oxide used was about 68 per cent of the polarization.

In the strontium process the strontium oxide was slacked with water and in boiling conditions the undiluted molasses was added, the mixing of molasses with hydroxide being continued until the proportion of strontium oxide to polarization was about 100 per cent. The mixture was boiled continuously and filtered through presses.

RESULTS—The mother liquor obtained from the saccharates in the three methods *before washing* was as follows:

PROCESS	BRIX	POLARIZATION
Lime	5.5	0.45
Barium	28.0	1.20
Strontium	30.0	0.00

After washing the saccharate, the following amounts of mixture of mother liquors and wash waters were obtained:

SACCHARATE	Per cent of Mixture	Sugar Average
Lime	1000	0.5
Barium	180	0.9 (1.3 pol.)
Strontium	250	0.4

It is remarkable that no raffinose could be detected in the concentrated mother liquor from either the calcium or the strontium saccharate, whereas in the concentrated mother liquor of 72 Brix and 11.8 polarization from the barium saccharate about 1.85 per cent raffinose was present. In the mixture, therefore, of mother liquor and wash water of polarization 1.3, from the barium saccharate, only 0.9 per cent sugar was present. In an article[1] published some years ago, it was shown that about 48 per cent of the total raffinose introduced by the molasses is eliminated in the mother liquors of the barium process.

The juices from the saccharates, after decomposition with carbon dioxide and filtering, were concentrated and analyzed with the following results:

	Calcium Saccharate Juice	Barium Saccharate Juice	Strontium Saccharate Juice
Brix	64.4	63.8	65.1
Polarization	59.1	62.5	63.7
Sugar	56.6	60.98	61.02
Raffinose	1.32	0.82	1.45
Raffinose on 100 pol.	2.24	1.32	2.28
Apparent purity	91.8	98.0	97.9
Real purity	87.9	95.6	93.7

In appearance the juice from the strontium saccharate showed less color than the other juices, being of a light straw color, the juice from the barium saccharate ranked second.

In calculating the yield of granulated sugar by the three methods, the sugar content of the molasses was taken as 48.5 per cent. The following percentages of the total sugar introduced were lost in mother liquors:

PROCESS	PER CENT
Calcium	5.00
Barium	1.62
Strontium	1.00

The residual percentages of sugar in the thick juices were then:

PROCESS	SUGAR Per cent	Purity
Calcium	48.5—5.00 = 43.50	87.90
Barium	48.5—1.62 = 46.88	95.60
Strontium	48.5—1.00 = 47.50	93.70

According to the formula

$$\frac{100}{\text{Purity Thick Juice}} \times \frac{\text{Purity Thick Juice} - \text{Purity Molasses}}{100 - \text{Purity Molasses}}$$

$\times$ 100, the extraction was as follows:

PROCESS	Sugar in Thick Juice Per cent
Calcium	81.40
Barium	93.79
Strontium	90.90

The sugar remaining in the molasses was then:

PROCESS	PER CENT
Calcium	16.6
Barium	6.0
Strontium	8.9

According to the practice followed in the lime process work, it would take six operations to complete the extraction of the sugar from the molasses, whereas in the barium and strontium processes three operations would be sufficient.

SUMMARY

1—The juices from barium and strontium saccharates are much lighter in color than those obtained from calcium saccharate, being in the proportions of 2.92, 2.25, and 8.60 color, respectively.

2—Of the 48.5 per cent original sugar in the molasses there were obtained:

PROCESS	As Granulated Sugar Per cent	Sugar in Molasses Per cent	Sugar in Mother Liquor Per cent
Calcium	35.45	8.05	5.00
Barium	43.97	2.91	1.62
Strontium	43.18	4.32	1.00

3—The peculiarity which raffinose has of being partly eliminated in the barium process is a great advantage over the calcium and strontium processes. At a certain factory during the last eight years, an average of 48.9 per cent of the raffinose present in the molasses introduced was eliminated in the mother liquor.

4—In the process of washing the saccharates, notwithstanding the decided alkaline reaction of the wash waters, a small amount of sugar goes into solution. This is most noticeable in the strontium waste waters. In the mother liquor of about 30° Brix, as it runs from the presses, usually no polarization is found, whereas the waste waters of about 7° Brix show as much as 0.7 polarization.

5—As regards extraction, the barium process is the most desirable. The strontium process is also more economical than the Steffen lime process, although the discarding of molasses is a drawback as it is in the Steffen process.

6—The mother liquors of the barium and strontium processes can be concentrated easily to 42 Bé., at which density they contain at least 12 per cent K_2O and 4 per cent nitrogen.

7—As regards the fear of barium or strontium compounds being present in the granulated sugar, there has not been found even the slightest trace of such compounds in the finished products, and all prejudice against the barium and strontium processes for this reason is baseless.

A patent on a process for manufacturing synthetic camphor from turpentine has been applied for by P. Giraudet of Louisiana. He claims that with this process camphor can be produced in ton lots and that 100 lbs. of turpentine will produce 50 lbs. of camphor.

---

[1] "Raffinose in the Barium Process," *Sugar.*

The Effect of Varying Hydrogen-Ion Concentration upon the Decolorization of Cane Juice with Carbon[1]

By Joseph F. Brewster and William G. Raines, Jr.

BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C., AND THE LOUISIANA SUGAR EXPERIMENT STATION, NEW ORLEANS, LOUISIANA

It has been pointed out by Wijnberg[2] that better decolorization of sugarcane juice may be obtained with Norit if the juice is rendered slightly acid. An acidity of 0.01 *N* is recommended, but what acid is to be used is not stated. Wijnberg further states that at 0.2 *N* to 0.33 *N* alkalinity decolorization with Norit sinks nearly to zero. Furthermore, Norit that has become saturated with the coloring matter of cane juice may be revivified to nearly its original activity by boiling with dilute alkali, whereby the coloring matters are dissolved.

The same author states that the pectins of cane juice are more readily adsorbed by Norit when the medium is slightly acid, and explains this action on colloid chemical grounds.

Further scientific explanation of this effect of acid in facilitating the decolorizing action of carbons is to be found in previous work in colloid chemistry. Perrin[3] states that the size of the particles of a colloid is a function of the reaction of the medium. Mayer, Schaeffer and Terroine[4] conclude that, in a very general manner, the addition of traces of acids to the solution of a negative colloid and of alkali to the solution of a positive colloid has the effect of increasing the size of the colloid particles. The addition of alkali to the first and of acid to the second produces the reverse. As examples, those authors state that Congo red, which is positive, becomes blue on the addition of acid, and at the same time the colloidal particles disappear. In suspensions of the phthaleins, which are negative colloids, addition of alkali renders them red and limpid. The same applies to suspensions of alkaloids, proteins, soaps, etc.

Holderer[5] found that the invertase of *Aspergillus niger* entirely passed through a porous clay filter when its solutions were neutral to phenolphthalein. When neutral to methyl orange the invertase was almost completely retained. Holderer states that the extraction of invertase from the mold is facilitated by making the water of maceration slightly alkaline.

There can be little doubt that the colloids and coloring matters of cane juice and sugar-house products are affected by acids and alkalies in a manner similar to the examples just cited, and it is very probable that these effects are produced by the concentration of hydrogen or hydroxyl ions in the medium.

Believing that the determination of H-ion concentration might find some important applications in the various processes of cane-juice clarification, the writers have done some preliminary work, the results of which are in part reported here. It is hoped that this may be continued and extended and a fuller report published.

In the course of experiments at the Louisiana Sugar Experiment Station in November and December 1920, the H-ion concentrations of many lots of normal cane juice were determined. The pH values found ranged from 4.8 to 5.8. These values seemed to have very little relation to the titratable acidity as it is usually determined. One lot of juice titrated 1.43 cc. 0.1 *N* per 10 cc. and had a pH value of 4.8. Another titrated 2 cc. 0.1 *N* and had a pH value of 5.0. The juice with the lower titratable acidity showed a slightly higher H-ion concentration. The acids of normal cane juice are organic acids little dissociated, so that slight increase or decrease of the quantities of these present would appear to have little effect on the pH value. In the case of abnormal cane, however, referring particularly to fermented cane, increase in H-ion concentration of the juice is to be expected as a result of the formation by organisms of stronger acids than those existing in normal cane.

EXPERIMENTAL PART

For the determination of H-ion concentrations of cane juice, the spot test was found more accurate and more rapid than any other colorimetric method. The indicators and buffer mixtures recommended by Clark and Lubs[1] were used, the buffer mixtures being checked with the potentiometer.

Fresh cane juice was expressed with the laboratory mill and clarified with kieselguhr. The juice, in 200-cc. portions, was acidified with 10 per cent acetic acid to the desired pH value, and the volume was adjusted to 220 cc. For neutralizing and for obtaining alkalinity *N* sodium hydroxide was used. For the decolorization tests, the 220 cc. of juice with pH value adjusted were treated with 2 g. of decolorizing carbon, brought to boiling, and filtered. When the liquid was cooled to room temperature the colorimetric readings were made with the Hess-Ives tint-photometer, and the color units and totals were determined from the table of Meade and Harris.[2]

The results shown in Table I were obtained by the use of different carbons. Color units left in the juice, as derived from Meade and Harris table, and total units divided by 3 are shown. The first set of figures were obtained in media weakly alkaline, neutral, and at two different degrees of acidity, respectively. The remaining figures were all obtained at varying acidities, from pH = 4 to about pH = 5. For comparison there are included colorimetric readings on the juice untreated with carbon.

TABLE I

		pH = 8	pH = 7	pH = 5.4	pH = 4	Juice Untreated with Carbon
A	Color Units: Red screen	23.4	8.3	18.6	11.6	57.7
	Green screen	44.4	24.7	27.3	22.2	104.4
	Blue screen	73.0	46.0	46.0	29.9	165.0
	$\frac{\text{Total units}}{3}$	46.9	24.12	28.07	21.2	109.0

		pH = 4.1	pH = 4.4	pH = 4.5	pH = 4.7	pH = 4.8	Juice Untreated with Carbon
B	Color Units: Red screen	8.3	11.6	16.2	19.8	21.0	54.2
	Green screen	19.8	32.6	29.9	31.2	32.6	98.9
	Blue screen	35.5	35.5	50.8	54.2	57.7	150.6
	$\frac{\text{Total units}}{3}$	21.2	26.6	32.3	35.1	37.1	101.2

		pH = 4.16	pH = 4.32	pH = 4.92
C	Color Units: Red screen	7.2	9.4	11.6
	Green screen	15.0	17.4	21.0
	Blue screen	24.7	24.7	28.6
	$\frac{\text{Total units}}{3}$	15.6	17.2	20.4
D	Color Units: Red screen	9.4	15.0	15.0
	Green screen	18.6	26.0	32.6
	Blue screen	28.6	32.6	29.9
	$\frac{\text{Total units}}{3}$	18.9	24.5	25.8

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *Intern. Sugar J.*, **17** (1915), 70.

[3] *J. chim phys.*, **1904–05.**

[4] *Compt. rend.*, **145** (1907), 918.

[5] *Ibid.*, **149** (1909), 1153.

[1] *J. Bact.*, **2** (1917), 1.

[2] THIS JOURNAL, **12** (1920), 688.

It is interesting to note under A that less total color was left at pH = 7 (neutrality) than at pH = 5.4, the natural acidity of the juice.

The rest of the figures demonstrate clearly that increase of H-ion concentration brings about increase of decolorization. These results may be duplicated by using phosphoric in the place of acetic acid.

In this connection, when working with increase of H-ion concentration in sucrose solutions it is necessary to take into consideration the fact that the rate of inversion of sucrose increases in proportion to increase in the concentration of hydrogen ion. The extent of inversion was determined at several pH values used in the decolorization tests. The results shown in Table II were obtained by boiling 200 cc. of juice under reflux after the H-ion concentration had been adjusted to the desired point by addition of acetic acid. The time factor for these inversions differs entirely from that of the decolorization tests, the experiments being made in the manner described more to accentuate the differences in rate of inversion with increase in pH value than to imitate the conditions of the decolorization experiments. At the end of 2 hrs.' boiling the juice was cooled, aliquot parts were taken, and the direct polarization was read after clarification with lead acetate.

In Table II are shown the H-ion concentration, the direct polarization after 2 hrs.' boiling, and the direct polarization of the original juice. This was 8.9° V. From these data were calculated the percentages indicated. The sample described in the first column under pH = 5 was the original juice without addition of acid. The loss of direct rotation here was 3.4 per cent of the original.

TABLE II—INVERSION OF SUCROSE

	pH = 5	pH = 4.8	pH = 4.6	pH = 4.4	pH = 4.2	pH = 4	Original Polarization
Direct polarization	8.6	8.5	7.0	6.5	6.6	5.0	8.9
Polarization per cent of original	96.6	95.5	78.6	73.0	74.2	56.2	...
Per cent loss	3.4	4.5	21.4	27.0	25.8	43.5	...

In view of the amount of inversion that can be brought about even at an acidity as low as pH = 5, about that of normal juice, it would appear to be somewhat doubtful that much advantage would be gained in practice by acidifying to improve decolorization unless conditions were very carefully controlled. Since fairly high acidity and a temperature at or near the boiling point of the juice are required for best results, the third factor to be controlled is that of time of exposure to high acidity. The authors have obtained good results by heating the juice mixed with carbon to the boiling point, adding phosphoric acid to an acidity of pH = 4, allowing a short time for action, and neutralizing back with milk of lime. Calcium phosphate precipitates out and is removed with the carbon by filtration. One must be careful not to over-lime the mixture and thus obtain an alkaline reaction. It is safe to stop the addition of lime at about pH = 6.5. By this procedure as good decolorization may be obtained as by carrying through the entire procedure at pH = 4.

The Iodine Numbers of Unsaturated Hydrocarbons and Cracked Gasolines[1]

By W. F. Faragher, W. A. Gruse and F. H. Garner

MELLON INSTITUTE OF INDUSTRIAL RESEARCH, PITTSBURGH, PENNSYLVANIA

The work here presented represents an attempt to clear up, in small part, at least, the uncertainties connected with the determination of the unsaturated constituents of cracked gasolines, and, if possible, to find the conditions under which unsaturation may be determined accurately. Such data are of interest, not only from the point of view of the derivatives obtainable, but also from that of the keeping qualities of a gasoline itself.

The methods ordinarily employed for this determination are, in the order of the frequency of their use, the sulfuric acid absorption method, the iodine number method, and the bromine absorption method. The sulfuric acid absorption method is the one most generally used, but it is practically useless from the standpoint of information obtainable, since sulfonation, polymerization, solution, and possibly oxidation occur along with the absorption of unsaturated compounds. The method has been standardized by Dean.[2]

The bromine absorption method[3] is least employed because of its inconvenience, and it is useful chiefly when it is desirable to determine substitution as well as addition.

The iodine number method is well known, chiefly in the field of animal and vegetable fats and oils. The literature on its use for mineral oils is scanty; for gasolines, the method has been standardized by Dean,[2] who was interested in getting a rapid and reproducible technique. The results obtained were found to depend entirely upon uniform procedure. Dean used the Hanus solution, a 30-min. reaction period, and a quantity of gasoline so chosen (depending on its unsaturation) that from 10 to 30 per cent of the reagent was absorbed. The weight of the gasoline varied from 0.04 to 0.20 g.

Smith and Tuttle[1] have determined iodine values of lubricating oils, using the Hanus solution and a 30-min. period of reaction. They believed it advisable to use as much as 1 g. of oil. This procedure gave a nearly constant value with slight variations in quantity of sample, but very low iodine numbers. Radcliffe and Polychronis[2] have studied the action of Hübl, Hanus, and Wijs solutions on heavy mineral oils. They found that the numbers obtained were in the order Hanus > Wijs > Hübl, though the Hanus and Wijs values agreed fairly closely. All three solutions gave increasing values over a 24-hr. period, and the character of the curves for the three solutions was about the same. Radcliffe and Polychronis discarded the Hanus solution because, in the first place, a difference of 20° C. in temperature caused a variation of 5 units in an iodine number of 30, and because they found that the presence of a slight excess of bromine produced a considerable change in the iodine number of an oil determined. The Hübl solution gave an iodine number much below the theoretical value for an amylene at the end of 2 hrs., while the Wijs solution gave a satisfactory number.

Röderer[3] has found that for heavy fractions of mineral and lignite tar oils the Hübl-Waller and Wijs solutions give maximum values, using five- to ten-fold excess of reagent and periods of 16 to 24 hrs.

Grün and Ulberich,[4] working with heavy fractions of lignite tar oils and using the Wijs reagent, found iodine numbers higher than the olefine content, as estimated by other reactions, would allow. They, therefore, took the bromine absorption and substitution numbers by the method of McIlhiney and found that the Wijs solution might give an iodine number of 27, while no bromine was added and 30 per cent of bromine was substituted.

---

[1] Presented before the Petroleum Section at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Bureau of Mines, *Technical Paper* **181**.

[3] McIlhiney, *J. Am. Chem. Soc.*, **21** (1899), 1084; Schweitzer and Lungewitz, *J. Soc. Chem. Ind.*, **14** (1895), 130.

[1] Bureau of Standards, *Technologic Paper* **37**.

[2] *J. Soc. Chem. Ind.*, **35** (1916), 341.

[3] *Z. angew. Chem.*, **33** (1920), 235.

[4] *Ibid.*, **33** (1920), I, 295.

PREPARATION OF MATERIALS USED IN TESTS

Since practically no information was available on the results of the use of the Wijs, Hanus, and Hübl solutions with hydrocarbons of low molecular weight, such as are found in gasolines, it seemed advisable to make comparative experiments with the two former reagents; the Hübl solution was not used.

HANUS SOLUTION—In order to check up the effect of excess bromine in the reagent, reported by Radcliffe and Polychronis, two Hanus solutions were prepared:

Hanus Solution 1, containing 12.7 g. of iodine and 2.88 cc. (= 9.00 g.) of bromine per liter of glacial acetic acid.

Hanus Solution 2, containing 12.7 g. of iodine and 2.56 cc. (= 8.00 g.) of bromine.

It will be observed that Hanus Solution 2 contains the atomic proportions of bromine and iodine required for a 0.1 *N* solution of iodine monobromide, while the Hanus Solution 1 contains the same amount of iodine but the excess proportion of bromine ordinarily used, 13.2 g. iodine and 3 cc. (= 9.36 g. bromine).[1] It is probable that the extra amount of each of the reagents was originally used to compensate for impurities present. The original suggestion of Hanus[2] was to prepare dry iodine monobromide and then to dissolve weighed amounts of it.

WIJS SOLUTION—Only one Wijs solution was prepared: 8.50 g. iodine + 7.80 g. iodine trichloride per liter of glacial acetic acid. These are the proportions for a 0.1 *N* solution of iodine monochloride, but it was found necessary to add more iodine trichloride in order to bring the titration value of the solution to the point where it was three times the value shown by the iodine solution before any ICl_3 had been added. For the particular sample of ICl_3 on hand, the proportions finally adopted were:

8.50 g. iodine
8.60 g. iodine trichloride

There is a great deal of misinformation in the literature on the proportions of materials to be used in preparing the Wijs reagent; this question has been commented on by Dubowitz[3] and by Weigemann and Kayser.[4] Since slight variations in the weight of iodine trichloride used do not affect the resulting iodine numbers, it is suggested that the best way of making up this solution is as follows: Use 8.50 g. of resublimed iodine per liter of glacial acetic acid, determine the value of the solution in terms of standard thiosulfate solution, and then add iodine trichloride until the titration value of the solution is three times as great as that of the solution of iodine only.

GASOLINES USED—Three gasolines were employed in this work:

Gasoline A—An unrefined fraction to 150° of a pressure distillate made from Pennsylvania gas oil by cracking at 550° C. at 100 lbs. pressure. The cracking apparatus was such that local superheating was entirely avoided. The color and odor of the fraction were good and the material was entirely stable on standing.

Gasoline B—An unrefined fraction to 150° of a pressure distillate produced commercially from a mid-continent oil in an ordinary pressure still. The exact pressure and temperature of the cracking process used are not known.

Gasoline C—An unrefined fraction to 150° of a pressure distillate made in a semi-commercial installation for vapor phase cracking. The pressure, temperature, and source of material are not known, but it is known that it was cracked for motor spirit rather than for unsaturated hydrocarbons and by-products, so that the pressure and temperature were probably low.

The degummed Gasoline B was prepared by allowing a stoppered bottle containing 100 cc. of the material to stand exposed to a northern light for 9 mo. About 1 cc. (1 per cent) of clear, viscous, brown oil deposited during this time, and the color and odor of the gasoline were improved very markedly.

All these gasolines were distilled through a 12-in. Hempel column filled with magnesium turnings.

HYDROCARBONS—The unsaturated hydrocarbons which were used in this investigation were prepared by different methods: amylene and isoprene from amyl alcohol, octylene from *sec*-octyl alcohol, heptine from heptaldehyde, and the other hydrocarbons from the corresponding saturated hydrocarbons.

The trimethyl ethylene (Amylene I) was isolated from amylene obtained from the Eastman Kodak Company by the method given by R. Adams.[1] The tertiary amyl alcohol obtained was dehydrated by means of anhydrous oxalic acid and carefully refractionated several times through a Vigreux column; the fraction used was that distilling from 36.3° to 37.3° C. (747 mm.).

After fractionating the Eastman amylene several times, a fraction distilling from 28.8° to 31.8° C. was collected. This fraction corresponds to unsymmetrical methylethylethylene (Amylene II).

Octylene was obtained from *sec*-octyl alcohol (methylhexylcarbinol) distilling from 174° to 176° C., by a number of different methods. The use of phosphorus pentoxide as dehydrating agent was found to give the best results. The octylene obtained was purified by fractionation and distilled finally at 122° to 124° C.

The hexylenes, *n*-hexylene and isohexylene, and heptylene were prepared from *n*-hexane, isohexane, and *n*-heptane, respectively, all isolated from straight-run Pennsylvania gasoline. The *n*-hexane and *n*-heptane were fairly pure specimens, but the isohexane was a fraction boiling from 63° to 65° C. Monochloro compounds were prepared from these hydrocarbons and separated by repeated fractionations from unchanged hydrocarbons and the more highly chlorinated products. The olefines were prepared from the chloro compounds by the method described in a previous paper.[2] The products obtained by the elimination of hydrogen chloride were subjected to repeated fractionations through a Vigreux column; fractions distilling over a 1° or 2° range were collected after four or five fractionations.

TABLE I

	Fraction Collected (760 Mm.) ° C.	Specific Gravity 20°/0°	IODINE NUMBER	
			Found	Calculated
Amylene I	36.3–37.3	...	354	362
Amylene II	28.8–31.8	. .	367	362
Isoprene	29.3–33.8	..	382	741
n-Hexylene	66–68	0.691	295.5	302
Isohexylene	64–65	0.684	309	302
Hexadiene	75–78	0.763	426	620
Cyclohexene	81–82	0.809	298	310
Cyclohexadiene	82–83	0.846	204	630
Heptylene	96–98	0.727	260	254
Heptadiene	100–105	0.796	253	518
Octylene	122–124	0.735	210	226
Cetene	125–145 (10 Mm.)	...	105	113

Hexadiene and heptadiene were prepared in a similar way from the dichloro compounds of *n*-hexane and *n*-heptane, but the products obtained were not as pure as the olefines, and undoubtedly were mixtures.

Cyclohexene and cyclohexadiene were prepared from the mono- and dichloro derivatives of cyclohexane.

The heptine used was kindly given by Prof. B. H. Nicolet, University of Chicago, and was pure *n*-heptine, $C_5H_{11}.C\equiv CH$.

---

[1] Hunt, *J. Soc. Chem. Ind.*, **21** (1902), 454; Tolman and Munson, *J. Am. Chem. Soc.*, **25** (1903), 244.

[2] *Chem. Zentr.*, **1901**, II, 1217.

[3] *Chem.-Ztg.*, **38** (1914), 1111.

[4] *Ibid.*, **39** (1915), 491.

[1] *J. Am. Chem. Soc.*, **40** (1918), 1950.

[2] W. F. Faragher and F. H. Garner, *Ibid.*, **43** (1921), 1715.

The isoprene, which was prepared from amyl alcohol through the dichloride, we owe to the kindness of Dr. E. F. Farnau, University of Cincinnati. It was refractionated before use and the fraction coming over from 29.3° to 33.8° was used.

In Table I are given the boiling points, specific gravities and maximum iodine numbers of the hydrocarbons used.

Experimental Details

For weighing out the volatile materials used, special weighing bottles, 10 mm. × 40 mm. and having glass stoppers with ground joints 15 mm. long, were made of Pyrex glass. On a warm day these weighing bottles lost a volatile material, say, amylene (b. p. 31°), at the rate of about 1 mg. in 3 min. By using ice baths and working quickly, these losses were minimized. The usual iodine absorption flasks made of Pyrex glass and fitted with ground glass stoppers were employed.

PROCEDURE—The procedure was as follows: The stopper of the weighing bottle containing the material to be examined was loosened, and the weighing bottle dropped into the absorption flask, which contained 10 cc. of carbon tetrachloride. After shaking the closed flask, 25 cc. of the reagent were run in from an automatic pipet, and the flask was set in the dark for the time period chosen. The reaction was stopped by adding 10 cc. of 10 per cent potassium iodide solution and 200 cc. of distilled water. Titrations were made with 0.1 *N* thiosulfate, starch solution serving as indicator. By following a rigid procedure, two observers could check one another closely, and one observer could check himself closely over long time periods. Thus on octylene at different quantity points:

Observer A obtained	208.7	212.4
Observer B obtained	209.0	210.0

The same observer obtained on a gasoline on August 17, 1920, 215.2, and on April 13, 1921, 215.2. A blank determination was made each day.

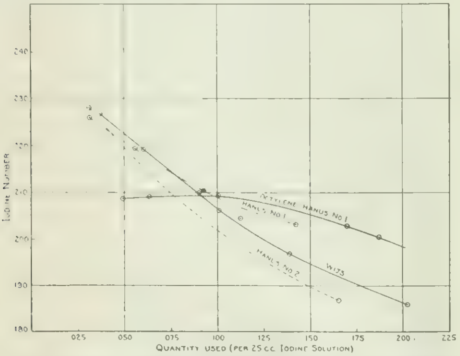


FIG. 1—QUANTITY CURVES FOR GASOLINE A-30 MIN., AND OCTYLENE

TABLE II (Fig. 1)

Period of contact with iodine solution in all cases = 30 min.

Hanus 1		Hanus 2		Wijs	
Amt.	Iodine Number	Amt.	Iodine Number	Amt.	Iodine Number
		Gasoline A			
0.0308	236	0.0308	238	0.0371	227
0.0567	219	0.0635	209	0.0605	219
0.0922	210	0.0904	209	0.1017	206
0.1422	203	0.1656	187	0.1154	205
				0.1389	197
				0.2028	186
		Octylene			
0.0493	208.7	0.0491	211.6	0.0489	211.7
0.0505	209	0.0499	210	0.0495	210.1
0.0994	208.8	0.1002	212.4	0.0975	209.8
0.1057	208.2	0.1000	210	0.1001	211
0.1707	203	0.1029	207	0.1586	211
0.1873	200			0.2194	203

The Hanus 2 and Wijs values for octylene are not shown on chart.

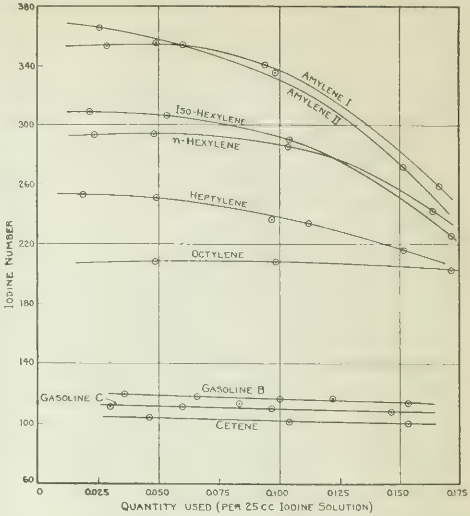


FIG. 2—QUANTITY CURVE FOR OLEFINES

TABLE III (Fig. 2)

Amt.	Iodine Number	Amt.	Iodine Number	Amt.	Iodine Number
Amylene I (Trimethylethylene) (10 min.)				*Amylene II* (*unsym*-Methylethylethylene) (10 min.)	
0.0279	354.5			0.0250	367
0.0603	354.5			0.0484	356
0.0936	341.5			0.0979	337
0.1666	258.0			0.1515	272
Hexylene (30 min.)		*Heptylene* (30 min.)		*Isohexylene* (30 min.)	
0.0231	294	0.0188	253	0.0221	309
0.0481	295.5	0.0499	251	0.0534	307
0.1051	285	0.0968	237	0.0971	288
0.1626	243	0.1307	215.5	0.1718	226
Octylene (30 min.)				*Cetene* (10 min.)	
0.0493	208.7			0.0472	105
0.0994	208.8			0.1028	101
0.1707	203			0.1529	101
Gasoline B (10 min.)				*Gasoline C* (10 min.)	
0.0371	120			0.0304	112
0.0687	118			0.0601	112
0.1023	115			0.0840	114
0.1214	117			0.0963	109.5
0.1547	112.5			0.1483	108

Fig. 1 shows the change with quantity[1] of the iodine numbers of cracked Gasoline A and of octylene for the two Hanus solutions and the Wijs solution. The scale used is rather large and emphasizes differences. For quantities below 0.1 g. all three solutions give practically the same result. The curve marked "octylene" represents the results for octylene with all three solutions—the three curves are identical. This would indicate that the differences between the three solutions for the gasoline are due to non-olefines, and may hold out the hope that a reagent will be found which will distinguish between olefines and other unsaturated components of cracked gasoline. The curve for octylene is practically flat in the working range, while the curves of the gasoline show decided slopes. From the following curves it will be apparent that the shape is more or less characteristic of the diolefines.

The theoretical iodine number for octylene is 226, while all of our solutions gave a value of 210 up to 0.1 g. used.

Following the recognition of the identity of results given by the two Hanus and the Wijs solutions, the Hanus 1 reagent was used in all subsequent work.

[1] The variation of quantity of hydrocarbon used affords a means of studying the effect of varying the excess of reagent employed

Fig. 2 shows the variation with quantity of the iodine numbers of a series of olefines of increasing molecular weights. It will be observed that as the molecular weight increases, the flat portion of the curve extends gradually over the whole experimental range—to 0.175 g. This may readily be explained by considering that for a given weight of olefine, the same quantity of reagent will be in much greater excess for a material of high molecular weight than for one of low molecular weight. In other words, a change of quantity over the whole experimental range does not for a high, molecular-weight olefine greatly change the molecular ratio of unsaturated material to reagent. For an olefine of low molecular weight there is, however, a large change in this ratio for the changes in quantity used; and as a result the usual quantity effect becomes apparent. The equilibrium point, which is the iodine value, drops off.

Of particular interest are the pairs of curves for two amylenes and for two hexylenes. The two sets of values lie so close together as to indicate that the influence of isomerism may for the time being be neglected. The differences in the maximum values may probably be traced to small amounts of impurities, while differences in the slopes of the curves may be attributed to a slight, but real, influence of isomerism.

Quantity curves are also given in Fig 2 for two types of cracked gasoline; Gasoline B, an ordinary pressure-still product, and a gasoline, made by cracking in the vapor phase for motor fuel. Both curves are as flat as that for cetene, and probably for the same reason—that the unsaturation is too low to permit the dropping off point to appear in the experimental range. These gasolines are known to have contained diolefinic, or gum-forming material, and these curves show that nothing concerning this constituent can be deduced from quantity curves.

TABLE IV (Fig. 3)[1]

Amt.	Iodine Number	Amt.	Iodine Number
Isoprene (10 min.)		*Hexadiene* (30 min.)	
0.0038	421	0.0084	426
0.0105	389	0.0234	382
0.0195	382	0.0440	332
0.0250	367		
0.0788	283	0.1091	251
0.1153	267	0.1398	227
0.1693	230	0.1781	193
Cyclohexene (30 min.)		*n-Heptine* (30 min.)	
0.0337	304	0.0101	243
0.0522	295.5	0.0289	241
0.1039	298	0.0574	239
0.1574	285	0.0840	236
		0.1240	233.5

[1] *n*-Hexylene and isohexylene as given for Fig. 2.

Fig. 3 gives quantity curves for two diolefines, one acetylene homolog and one cyclic unsaturated compound, cyclohexene.

The change with quantity of the iodine value of the diolefines is very striking, and the form of curve is quite distinctive. The isoprene curve, which is more complete, is distinctly cubic with one point of inflection. The one for hexadiene, as far as followed, takes the same form. The maximum values at 0.01 g. lie about 425, while the theoretical value for isoprene is 741 and for the hexadiene 630. Evidently, one double bond of the diolefine is easily attacked by the reagent, and the other less easily. The ranges in which these reactions are respectively most important may be related to the shape of the curve. Thus, at concentrations lower than that at the point of inflection, saturation of both double bonds may occur simultaneously, thus accounting for the rapid rise in the curve; while at points beyond the point of inflection only one double bond is much affected, and this reaction proceeds like that of an olefine, the curve resembling that for *n*-hexylene. These suggestions might be restated in terms of the theory of conjugated double bonds, but as the structure of the hexadiene used is uncertain, no attempt is made to do so here.

The curve for normal heptine is very interesting. The material was quite pure, judging from its method of preparation, yet the maximum value obtainable was 243, as against the theoretical value of 536; allowing for a contamination due to polymerization on standing, this would indicate a half value as the maximum; the only explanation seems to be that the compound to which two iodine atoms have added, $RCI=CHI$, is saturated so far as the Hanus reagent is concerned. $RCI=CHI$ is more likely to act in this way than the possible tautomer, $RCH=CI_2$. The acetylenes and diolefines are unsaturated to the same extent, but the contrast in the shape of the curves is most marked; in one case the two iodine molecules add on to two different pairs of carbon atoms, but with the heptine there is apparently no tendency for the addition of two iodine molecules to the *same* pair of carbon atoms. The curves for normal and isohexylene are the same as for Fig. 2, and are reproduced for comparison with the diolefines. The curve for cyclohexene does not drop off with increase in quantity as do the open chain hexylenes. Apparently a smaller excess of reagent is required to carry the reaction to the theoretical maximum than for the other hexenes—the cyclohexene is "more unsaturated" from an empirical viewpoint.

The iodine numbers for these hexene compounds, as measured, lie very close to the theoretical.

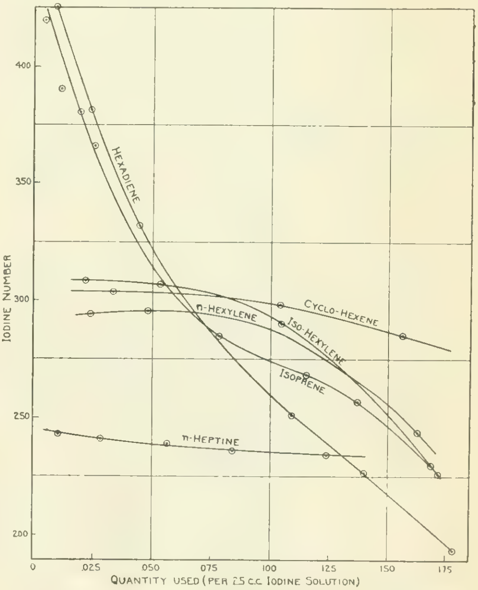


FIG. 3—QUANTITY CURVES FOR DIOLEFINES AND OTHER UNSATURATED COMPOUNDS

The amounts used were approximately the same in each set of experiments (in order to avoid the effect produced on the iodine number by changing the quantity). The amount of hydrocarbon was so chosen that a 50 per cent excess of reagent remained unabsorbed at the end of an experiment, except in one case (Amylene I, Table V) where a 35 per cent excess gave numbers within 6 per cent of the theoretical and within 3 per cent of that obtained with very large excesses.

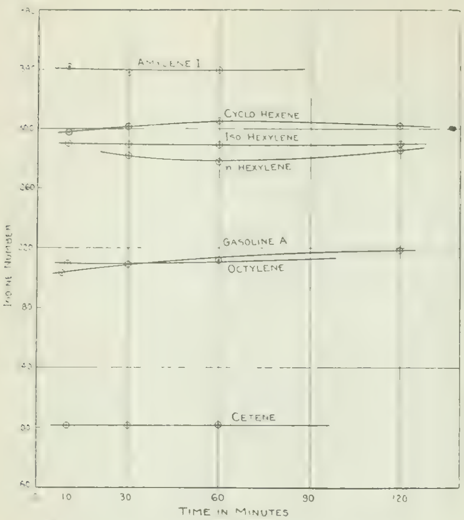


Fig. 4—Time Curves, Iodine Numbers of Olefines

Table V (Fig. 4)

Time	Iodine Number	Time	Iodine Number	Time	Iodine Number
Amylene I		*Cyclo-Hexylene*		*Iso-Hexylene*	
10	341.5	10	298	10	290
30	337.5	30	303.5	30	290
60	340	60	300.5	60	288
		120	300.5	120	290
n-Hexylene		*Octylene*		*Cetene*	
10	287	10	210	10	101
30	284	30	209	30	101
60	278	60	210	60	101
120	285				

Time	Iodine Number
Gasoline A	
10	204
30	210
60	215
120	218

Fig. 4 illustrates the influence of time on the reaction with olefines. It will be observed that the curves are quite flat. This indicates clearly that for all the olefines employed, including straight, branched-chain and cyclic compounds, containing secondary and tertiary hydrogen atoms, the substitution reaction is negligible.

On this chart is placed also the time curve for Gasoline A; the change in iodine number with time is quite apparent up to the 60-min. point. As the curve is flat after this point, it is apparent that substitution is negligible. The shape of the curve is characteristic of the diolefines, as will be apparent from Fig. 5. It may be noted that this gasoline deposited no gum over 9 mo. and maintained its unsaturation figure exactly over that time.

Table VI (Fig. 5)

Time	Iodine Number	Time	Iodine Number	Time	Iodine Number
Hexadiene		*Isoprene*		*Heptadiene*	
10	301.5	10	283	10	209
30	332	30	301	30	237
60	347	60	306	60	244
120	349	120	327	120	253
Heptine		*Cyclohexadiene*		*Gasoline B-Degummed*	
10	231.5	10	155	10	93
30	236	30	194	30	98
60	239	60	197	60	99.7
120	238.5	120	204	120	107

Fig. 5 gives the change with time of the iodine numbers of the diolefines and the one acetylene homolog used. For the diolefines the behavior is quite uniform; the value increases gradually to 60 min. and then remains constant. The values attained lie, in general, at about half the theoretical value of the diolefine in question. At a fixed concentration the reaction would be expected to proceed to a constant value corresponding to the saturation of one of the double bonds, since the quantity curves indicate that only one double bond is attacked as long as large excesses of reagent are not present. The contrast of these curves to the entirely flat curves of the olefines is marked.

The curve for the heptine is as striking as its quantity curve; it has a shape approximating to that of an olefine; the indication is that it really functions as an olefine, becoming saturated after the equivalent of two iodine atoms have added to the triple bond.

The curve for the degummed Gasoline B shows the form characteristic of the diolefines, this fact is of interest because it is ordinarily supposed that the diolefine content and the gum-forming content of a cracked gasoline are very closely related. If it should be possible to establish that the gum-forming constituents have not been completely removed, the apparent conflict might be explained.

Attention may be called to the striking indications that the Hanus solution does not cause substitution in any of the classes of hydrocarbons worked with. This may safely be deduced from the fact that the values as determined did not increase with long time periods, and from the fact that large excesses of reagent in no case gave values higher than those calculated from the structure of the compounds in question. In order to check the question of substitution with compounds ordinarily regarded as saturated, experiments were made with very pure hexane, cyclohexane, benzene, and xylene. All these compounds were found to be quite unattacked.

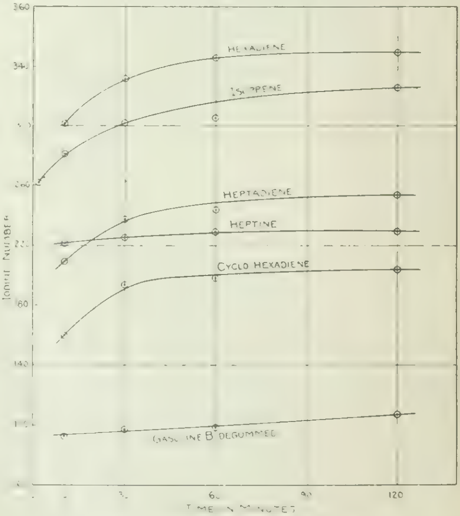


Fig. 5—Time Curves, Iodine Numbers of Diolefines

From the work of Grün and Ulberich it might be supposed that with the Wijs solution substitution undoubtedly does occur. The authors have not checked this matter as closely with the Wijs as with the Hanus reagent, but an experiment with the bromine method of McIlhiney on the sample of cetene used in this work indicates that the discrepancies of

Grün and Ulberich are due to the fact that the bromine, as dissolved in carbon tetrachloride, is not absorbed to the full extent of the unsaturated groups present.

	Cetene I	Cetene II
Theoretical bromine number	80	80
Bromine number found	41	0
Theoretical iodine number	113	113
Iodine number found	105	105

In general, bromine should be far more active in substitution than iodine, which confirms this point.

It was hoped that this work would permit the tracing of a connection between the gum-forming constituents of a gasoline and the diolefine content. This has not been possible; time curves for Gasoline A, which formed no gum, the degummed Gasoline B, and a fresh gasoline resembling B, which afterward deposited gum (this curve not given here) are all of the same, characteristic diolefine shape. It has been noted that the deposition of 1 per cent of gum changed the iodine number of Gasoline B from 118 to 93, about 20 per cent. This change would indicate that the gum-forming constituents are highly unsaturated substances, possibly diolefines, which cause the large change in iodine value because of their low concentration. This is indicated by the curves on Fig. 3.

Possibly a study of the iodine numbers before and after some type of refining treatment will permit a prediction as to the gumming properties of a gasoline; the writers have planned a study of this question.

CONCLUSIONS

1—The Hanus and Wijs reagents give the same results with olefines, and with cracked gasolines for amounts below 0.1 g.

2—The Hanus reagent as ordinarily made up gives results with olefines which indicate the true unsaturation. A small variation in the excess of bromine employed does not change the results.

3—Diolefines may be qualitatively recognized by the shape of the time and quantity curves. On increasing the excess of iodine present very largely, iodine numbers approaching the theoretical values are obtained.

4—*n*-Heptine functions as an olefine, only one pair of halogen atoms being added. This is probably typical of acetylenes in general.

5—The Hanus solution does not cause any appreciable substitution of hydrogen in the molecules of simple paraffin, cycloparaffin, or aromatic hydrocarbons, or of straight, branched-chain or cyclic olefines, of diolefines, acetylenes, or cracked gasolines.

6—Judging by the shape of the time and quantity curves obtained all the gasolines used contained diolefines. No direct connection has yet been traced between the gum-forming constituents of cracked gasolines and the diolefine content as indicated by the shape of the time and quantity curves.

Contribution to the Estimation of H-Acid[1]

By Henry R. Lee

RESEARCH LABORATORY, NEWPORT CO., MILWAUKEE, WISCONSIN

The stability of diazo compounds has been the subject of numerous researches. Most investigators have been interested chiefly in studying the type of the reaction, *i. e.*, whether of the first or second order, etc. For this reason they have worked at temperatures which would show a comparatively rapid rate of decomposition. Hantzsch[2] found that at 25° C. the rate of decomposition of diazobenzene was approximately eight times as rapid as that of *p*-diazotoluene. Cain and Nicoll[3] have shown that substitution of CH_3, ortho to the amino group, decreases the stability of the diazo compound, while a para substitution results in increased stability. This laboratory has been interested in the stability of diazo compounds from the standpoint of their use as standard volumetric solutions, and has made use of the monomolecular equation only as a means of verifying the results obtained.

Diazo salts show very great differences in their power to resist decomposition by hydrolysis. Many decompose rapidly at a low temperature, while others are comparatively stable even at the boiling point.

The choice of a diazo salt to be used as a standard solution for the estimation of the hydroxyl group should depend on the following considerations:

1—The stability of the salt in the solution in which it is prepared, and in which it is to be used.

2—The completeness of couplings of the salt with the intermediate in question.

3—The rate of coupling.

The method which has been used most generally in the past for the determination of the stability of diazo compounds consists in titrating, from time to time, a portion of the diazo solution with a standard solution of β-naphthol or β-naphthol-6-sulfonic acid (Schaeffer salt). This method was applied to the titration of H-acid to compare diazobenzene and *p*-diazotoluene with regard to their respective rates of decomposition.

EXPERIMENTAL

TITRATION—Four-hundredths *N* diazobenzene and diazotoluene solutions were prepared (as later described) using 3.5 moles excess hydrochloric acid. These solutions were kept at 0° C., and protected from light. At certain intervals samples of the diazo solutions were pipetted into jacketed burets and titrated into a standard H-acid solution. Table I presents the results obtained.

TABLE I—COMPARATIVE STABILITY OF DIAZOBENZENE AND DIAZOTOLUENE IN HYDROCHLORIC ACID SOLUTION

	PERCENTAGE DECOMPOSITION	
TIME Hrs.	DIAZOBENZENE (Curve 1)	DIAZOTOLUENE (Curve 3)
2	0.25	0.00
5	1.70	0.10
24	5.33	0.55
50	12.30	0.90
72	17.00	1.10
100	22.40	1.73
144	29.70	2.50

Results of this character are best expressed by means of a curve, as experimental errors can be more correctly distributed. Curves 1 and 3 present these data. (The curves have not been drawn through all the points, but are drawn to make the most symmetrical curves possible for the points determined.) Hantzsch has shown that at temperatures above 25° C. the decomposition of a diazonium salt is a monomolecular reaction. To test the order of the reaction at 0° C., substitutions were made in the monomolecular equation:

$$C = \frac{2.3}{t} (\log_{10} V\alpha - \log_{10} (V\alpha - Vt))$$

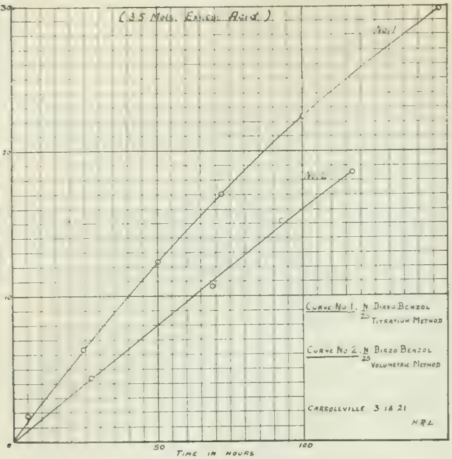
The following values for C were obtained from the curves:

---

[1] Presented before the Division of Dye Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *Ber.*, **33** (1900), 2517.

[3] *Chem. Zentr.*, **1902**, II, 1449.



Stability Curves for Diazobenzene in Acid Solution

Time Hrs	Diazobenzene (Curve 1)	Diazotoluene (Curve 3)
50	0.0000440	0.00000292
100	0.0000415	0.00000292
144	0.0000396	0.00000292

In the case of diazobenzene, the decreasing value obtained for C does not indicate a strictly monomolecular reaction. The amount of decomposition in the case of diazotoluene was so small that the means of measuring it were inaccurate. For these reasons the titration method does not appear suitable for exact work, particularly where the amount of decomposition is very small. Furthermore, the secondary reactions taking place between the diazo salt and the alkali used to effect coupling frequently introduce a considerable error.

MEASUREMENT OF NITROGEN EVOLVED—The scheme of keeping the diazo solutions at constant temperature and measuring the amount of nitrogen evolved was next studied.

Two hundred fifty cc. of 0.04 *N* diazobenzene and of diazotoluene were each placed in tightly stoppered sulfonation flasks provided with a mercury-sealed agitator. The nitrogen evolved was measured over water in a nitrometer. The diazo solutions were kept at 0° C. by means of an ice bath, and were protected from light. The results are presented in Table II.

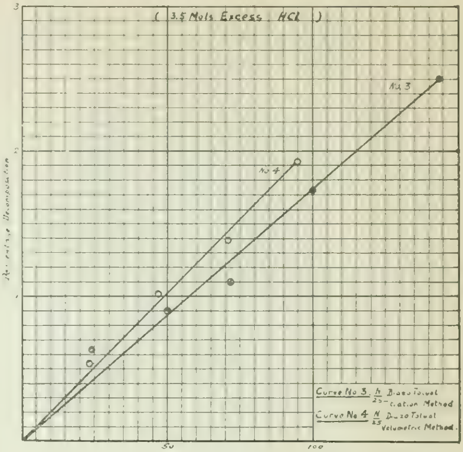
Table II—Comparative Stability of Diazobenzene and Diazotoluene in Acid Solution by Volumetric Method

Time Hrs	Percentage Decomposition	C	Average Value of C
		Diazobenzene	
27	4.4	0.0000295	
45	7.2	0.0000278	
69	10.8	0.0000271	0.0000286
93	15.2	0.0000295	
117	18.5	0.0000294	
		Diazotoluene	
23	0.55	0.00000389	
47	1.02	0.00000352	
71	1.49	0.00000360	0.00000360
95	1.92	0.00000340	

The values obtained for C were taken from the points determined and not from the curves. The relative stability of these two diazo salts is expressed by the ratio:

$$\frac{C_B}{C_T} = \frac{0.0000286}{0.0000036} = 1 : 7.94$$

In other words, the rate of decomposition of diazotoluene in acid solution at 0° C. is roughly one-eighth that of diazobenzene under similar conditions. The ratio which Hantzsch obtained at 25° C. was 1.0 : 7.91. This shows conclusively that the ratio C_B/C_T is constant over wide ranges of temperature. The rate of decomposition determined by Hantzsch at 25° C. is 24.5 times as rapid as that obtained at 0° C., for the two diazo salts studied.



Stability Curves for Diazotoluene in Acid Solution

RATE OF DECOMPOSITION IN ALKALINE SOLUTION—Diazobenzene and diazotoluene solutions prepared as described above were made alkaline with four moles excess sodium carbonate, and the rate of decomposition determined.

Table III—Comparative Stability of Diazobenzene and Diazotoluene in Alkaline Solution
(4 moles excess Na_2CO_3)

Time Hrs.	Percentage Decomposition	C	Average Value of C
		Diazobenzene (Curve 5)	
4	1.21	0.0000504	
23	5.98	0.0000446	0.0000456
28	7.18	0.0000443	
47	11.58	0.0000439	
		Diazotoluene (Curve 6)	
20	3.59	0.0000303	
27	4.87	0.0000308	
44	7.70	0.0000303	0.0000299
51	8.87	0.0000290	
68	11.15	0.0000289	

In both cases decreasing values of C were obtained in alkaline solution. This is in all probability due to the gradual coupling taking place between the diazo salt and the phenol or cresol resulting from the decomposition, thus decreasing the residual diazo compound.

For purposes of comparison the average value of C and the ratio C_B/C_T were determined:

$$\frac{C_B}{C_T} = \frac{0.0000456}{0.0000299} \text{ or } 1 : 1.52$$

The greater stability of *p*-diazotoluene both in acid and alkaline solutions having been established, the question of the completeness of coupling was considered.

A sample of commercial H-acid was recrystallized several times and vacuum dried, and its purity was determined by the diazotoluene and diazobenzene methods.

Analysis of Recrystallized H-Acid

Nitrite Titration	Kjeldahl Nitrogen Calculated to H-Acid (368)	OH Diazotoluene, 0.04 *N*	OH Diazobenzene 0.1 *N*
97.40	97.63	96.63	100.15
97.68	97.63	96.77	99.05
			99.71

On account of the greater solubility of chromotropic acid (which would be the only impurity present which would raise the coupling value above the amino value), it is evident that a recrystallized H-acid should not show a hydroxyl titration higher than the amino value. In this case diazobenzene showed an average OH titration 2.09 per cent higher than the amino value, and 2.93 per cent higher than the diazotoluene titration. These data tend to show that diazobenzene does not yield the correct coupling value.[1]

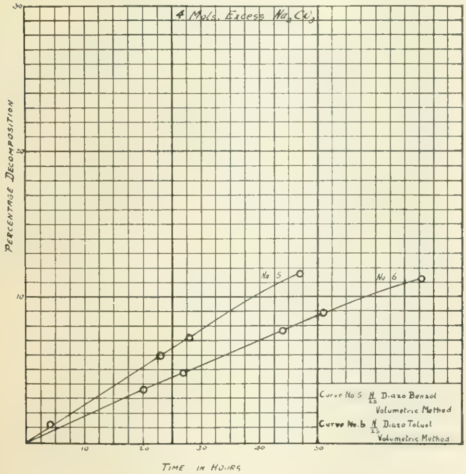
The analyses of a large number of samples of commercial H-acid show even more striking differences between the OH titration by the diazobenzene and diazotoluene methods.

Table IV summarizes the results from a series of eighteen samples run in duplicate by both the analytical and plant laboratories. Both laboratories worked independently on portions of the same dilution of H-acid and with portions of the same diazo solutions. The average differences in percentage show that it is much easier to obtain check results with diazotoluene than with diazobenzene.

Table IV—Comparison of Diazobenzene and Diazotoluene Methods for Analysis of Commercial H-Acid

Batch No.	NH_2 Per cent	Diazobenzene Anal. Lab. Per cent OH	 Plant Lab., Per cent OH	 Per cent Difference	Diazotoluene Anal. Lab., Per cent OH	 Plant Lab., Per cent OH	 Per cent Difference
6354	79.93	79.45	80.56	1.11	74.67	74.82	0.15
6355	79.28	79.82	79.45	0.37	73.93	73.93	0.00
6356	79.45	79.45	80.38	0.93	74.97	74.97	0.00
6357	79.03	79.45	80.56	1.11	75.11	75.11	0.00
6359	82.12	82.75	83.12	0.37	77.49	77.64	0.15
6360	78.19	78.54	80.19	1.65	73.63	73.48	0.15
6361	78.65	77.63	79.09	1.46	73.93	73.63	0.30
6362	80.80	81.65	80.92	0.73	77.49	77.49	0.00
6364	80.37	80.01	80.19	0.18	75.71	76.00	0.29
6366	82.87	81.65	82.75	1.10	76.00	75.71	0.29
6367	77.31	79.09	79.82	0.73	73.63	73.63	0.00
6368	82.24	82.39	82.39	0.00	76.45	76.30	0.15
6369	81.95	83.12	83.49	0.37	78.68	78.38	0.30
6370	85.61	86.42	86.05	0.37	81.05	81.05	0.00
6374	86.05	86.42	84.58	1.84	81.94	82.24	0.30
6375	84.30	84.58	84.95	0.37	80.16	80.75	0.59
6376	86.92	84.95	84.22	0.73	83.43	83.13	0.30
6381	84.74	87.33	87.51	0.18	81.35	81.35	0.00

Average difference in percentage by diazobenzene method = 0.75
Average difference in percentage by diazotoluene method = 0.16



Stability Curves in Alkaline Solution

The average difference between diazobenzene and diazotoluene analyses was 4.87 per cent. The above results show an average over-fusion of 0.5 per cent by the diazobenzene method and an average under-fusion of 4.37 per cent by the diazotoluene method. The titration with diazotoluene proceeded more rapidly and to a more definite end-point.

Preparation of Solutions and Method of Analysis

The best grade of commercial *p*-toluidine is recrystallized from ethyl alcohol (to remove the last traces of *o*-toluidine), dried in vacuo, and dry distilled. The constant boiling middle fraction is used for the preparation of the diazo solution and is considered C. P. (b. p. 199.9°–199.95° C. at 757.7 mm.).

preparation of 0.04 *N* *p*-diazotoluene—A stock solution of *p*-toluidine hydrochloride is prepared by dissolving 10.7082 g. of pure *p*-toluidine in 40 cc. of C. P. concentrated HCl (4.5 moles), and sufficient water to make up to one liter. One hundred cc. of this stock solution are pipetted into a 250-cc. volumetric flask. The flask is cooled by surrounding it with an ice and salt mixture until the contents are frozen. From a pipet are then added 102 cc. of 0.1 *N* nitrite (2 per cent excess). The ice within the flask is sufficient to counteract the heat of reaction and maintain a temperature of 0° to 2° C. The solution is allowed to stand 30 to 40 min., diluted to the mark with ice water and thoroughly shaken. The solution is kept at 0° and protected from light. (This method of preparing diazo solution is found to be much more rapid and to give more uniform results than titrating the amine with nitrite in a beaker and then making up to volume.)

Ten grams of press cake or 5.0 g. of dry H-acid are weighed accurately and dissolved in 400 cc. of water and sufficient sodium bicarbonate to give a clear solution, and made up to volume in a 500-cc. volumetric flask.

titration—Twenty-five cc. of the above solution are pipetted into a 600-cc. beaker, 200 cc. of ice water are added, and 2 g. of sodium bicarbonate. This solution is placed under a mechanical agitator and cooled with an ice bath to 0° to 5° C. The diazo solution is added from a jacketed buret, cooled with ice. When the titration is almost finished, approximately 2 g. of Na_2CO_3 are added, to speed up the rate of coupling. From 10 to 15 g. of salt are added near the end-point, and the titration is carried to the point where a spot test on filter paper gives a faint purple ring, when spotted against H-acid. If the purple color develops again (when tested as above described) after the solution has stood 5 min. the titration is finished.

Conclusions

1—The rate of decomposition of diazobenzene is approximately eight times as rapid in acid solution, and 1.5 times as rapid in alkaline solution, as that of *p*-diazotoluene.

2—The rate of coupling of diazotoluene is slightly more rapid than that of diazobenzene, and the secondary coupling, which is marked in the case of commercial samples of H-acid titrated with diazobenzene, is very slight when coupled with diazotoluene. This results in a more rapid coupling and a much more definite end-point.

3—The use of *p*-diazotoluene is recommended in the estimation of the coupling value of H-acid, Gamma acid, J-acid, S-acid, and other naphthol- and aminonaphthol-sulfonic acids.

On account of the great interest in the Boxing and Crating course given at the Forest Products Laboratory, Madison, Wis., additional courses will be given as follows: November 7–12, 1921; January 9–14, 1922; March 6–11, 1922; and May 1–6, 1922. The course is essentially a practical demonstration of such points as the characteristics of different styles of boxes and crates, the importance of nailing, the advantages of using dense woods, the efficiency of metal straps, the effect of moisture and change of moisture conditions in lumber on the strength of boxes and crates, tests on wire bound boxes, methods of improving the design of fiber board boxes, etc. The making of drum tests, drop tests, compression tests, and various others has proved efficient in driving home the principles of container construction.

---

[1] It should be kept in mind that in carrying out the diazobenzene titrations an attempt was made to conform to the method of analysis used by most manufacturers of H-acid. The H-acid was dissolved in 5 per cent sodium carbonate solution and titrated to a 5-min. end-point with 0.1 *N* diazobenzene.

Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis[1]

By G. L. Kelley and E. W. Evers

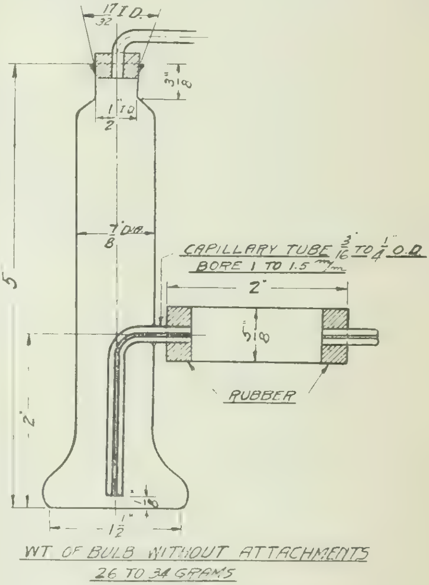
Chemical Laboratory, Midvale Steel & Ordnance Co., Nicetown Plant, Philadelphia, Pa.

A solution of potassium hydroxide has long been used as an absorbent for carbon dioxide in the determination of carbon by combustion. Bulbs filled with such a solution were capable of absorbing completely about 1 g. of carbon dioxide. This absorbent has been partly superseded in recent years by soda lime, which in the various bulbs used for the purpose would absorb from 1 to 4 g. of carbon dioxide, depending upon the capacity of the bulb. In an earlier article,[2] one of us described an absorption tube devised by H. L. Frevert, and a new absorbent for carbon dioxide called by the writer "soda-asbestos." This material was capable of absorbing about 20 per cent of its weight of carbon dioxide, which in the different types of bulbs used as containers amounted to from 6 to 15 g. of carbon dioxide. The reagent would be prepared from cheap grades of asbestos having a market price of about $150.00 per ton, and technical grades of sodium hydroxide, by heating a moistened mixture of these materials. Since the appearance of this article, Stetser and Norton[3] have described apparatus for the determination of carbon in steel, and give their experience with a modified variety of "soda-asbestos" which they have devised. The absorption tube which they have proposed differs from the Frevert tube only in its proportions.

Stetser and Norton recommend the use of their product without any additional material to absorb water. The writers have not considered this a safe procedure to employ with "soda-asbestos." When the mixture of sodium hydroxide and asbestos is practically free from water, its effectiveness as an absorbent is much less than when a small amount of water is present. The freshly prepared mixture gives up its water very slowly, but as the saturation of the bulb is approached, the water is released in increasing amount. Accordingly, in working with "soda-asbestos" we have placed a layer of calcium chloride at the exit end of the tube. Owing, however, to the variable and uncertain character of calcium chloride as a dehydrating agent, even this device has not been found capable of yielding uniformly accurate results. U-tubes of phosphorus pentoxide placed before and after the absorbing tube show a small loss of water by the latter, amounting to about 1 mg. in the course of a determination of carbon. For the purpose of securing greater uniformity in results, the authors now use phosphorus pentoxide as a drying agent.

The Frevert bulb as originally made up did not provide for the use of phosphorus pentoxide, but it has been possible to use this material as a drying agent by attaching a short tube to the outlet of Frevert's bulb. The tube is provided with a small one-holed rubber stopper at each end, which permits recharging with P_2O_5 without disturbing the carbon dioxide absorbent. A U-tube containing P_2O_5 is placed before the absorbing tube, and the outlet of the latter is connected with a bubble counter containing barium hydroxide. This device serves to indicate the rate of gas flow as well as the saturation of the sodium hydroxide. The accompanying figure shows the Frevert bulb with the phosphorus pentoxide tube attached.

While endeavoring to improve "soda-asbestos" as an absorbent for carbon dioxide the authors decided to test the properties of sodium hydroxide for this application. It was supposed that lack of surface would seriously interfere, but it was found that it would absorb nearly one-third of its weight of CO_2. Coarsely broken sticks of sodium hydroxide do not absorb as much as the powdered form, but the latter is objectionable because it cakes. The most satisfactory results were obtained with a material which would pass a 5-mesh screen, but remain on a 20-mesh screen. Grinding and sifting the sodium hydroxide, especially in moist weather, is very unsatisfactory. It is possible to buy small cans of "household lye" in which the sodium hydroxide is somewhat smaller than rice, and which has been found to serve our purposes admirably. This has proved to be far superior to either soda-lime or "soda-asbestos."



It has been pointed out to the authors that W. R. Fleming[1] has stated that solid sodium hydroxide may be used as an absorbent for CO_2 in the bulb covered by this patent. We believe, however, that this is the first report on its actual application in the absorption of carbon dioxide in connection with the determination of carbon in steel by combustion. Our experience with this reagent as used for this purpose is based upon its use in a large technical laboratory where several thousand determinations were made in each month over a period of more than a year. Potassium hydroxide would, of course, serve equally well, and it would have the advantage that water is retained better by potassium hydroxide than by the corresponding sodium compound, but it is more expensive and the difficulty of protecting it from moisture during preparation is even greater. A further disadvantage lies in the higher atomic weight of potassium.

---

[1] Received April 8, 1921.

[2] This Journal, **8** (1916), 1038.

[3] *Iron Age*, **102** (1918), 443.

[1] U. S. Patent 1,324,763.

The Determination of Chromium in Ferrochromium by Electrometric Titration[1]

By G. L. Kelley and J. A. Wiley

Chemical Laboratory, Midvale Steel & Ordnance Co., Nicetown Plant, Philadelphia, Pa.

A paper on the determination of vanadium and chromium in steel was published by Kelley and Conant,[2] and more recently a paper by Kelley and other collaborators[3] describes the determination of vanadium and chromium in ferrovanadium. In these cases the end-point was determined electrometrically. The present paper describes a method for the determination of chromium in ferrochromium in which the end-point in the titration is taken as the point of greatest change in the oxidation-reduction potential during the titration of the chromic acid with ferrous sulfate. The description of apparatus suited to this determination has been given by Kelley, Adams and Wiley.[4]

Standard Solutions

POTASSIUM DICHROMATE SOLUTION—5.6586 g. of the recrystallized and fused salt in enough water to make one liter.

FERROUS AMMONIUM SULFATE SOLUTION—47 g. of ferrous ammonium sulfate and 100 cc. of sulfuric acid (sp. gr. 1.58) in enough water to make one liter. This should be standardized daily by comparison with the dichromate solution which is used as the standard of reference.

HYDROCHLORIC ACID SOLUTION—One part of concentrated acid and three parts of water.

SILVER NITRATE SOLUTION—2.5 g. of silver nitrate in enough water to make one liter.

AMMONIUM PERSULFATE SOLUTION—100 g. ammonium persulfate and water enough to make one liter.

Method

Use a nickel crucible of about 60-cc. capacity, preferably free from manganese. Fuse 20 g. of sodium carbonate in the crucible, and during cooling rotate it in such a manner as to produce a lining on the crucible. When cool, place 16 g. of sodium peroxide in the crucible. Make a hole in the center of this and place in it 1 g. of ferrochromium, ground to pass a 100-mesh sieve. Mix the ferro-alloy with the peroxide by stirring with a stiff platinum wire, taking care that the alloy does not sink to the bottom. Fuse over a blast lamp until fusion is complete, and apply heat enough to maintain the melt in a state of quiet fusion for 3 min., rotating gently meanwhile. Avoid fusing the lining as this is detrimental to the crucible. During cooling, cause the molten mass to flow in thin layers on the surface of the crucible. When cold, wipe the outside of the crucible clean, and place it in 300 cc. of water contained in a 600-cc. beaker. Warm to complete the solution of the mass, and remove the crucible after rinsing. Boil the solution at least 30 min. Cool to room temperature, and add gradually 80 cc. of sulfuric acid (sp. gr. 1.58). Boil 5 min., cool, filter through asbestos, and make the volume up to exactly 1 liter. Analyze the solution as soon as it is prepared. Remove a 100-cc. portion, add 25 cc. of sulfuric acid, and titrate electrometrically with ferrous ammonium sulfate and potassium dichromate.

A modification of the method involves the following procedure: To 100 cc. of the solution, add 25 cc. of sulfuric acid, 10 cc. of silver nitrate solution, and 40 cc. of ammonium persulfate solution. Boil 10 min. after the permanganic acid color appears. Then add 5 cc. of 1:3 hydrochloric acid, boil an additional 5 min., cool, and titrate electrometrically with ferrous sulfate.

For the highest accuracy, the potassium dichromate should be recrystallized and fused. The dichromate solution is of such strength that each cubic centimeter corresponds to 2.00 per cent of chromium in a 0.10-g. sample. To calculate, multiply by 2 the cubic centimeters of dichromate solution to which the ferrous sulfate solution used is equivalent. This gives the result directly in per cent.

Vanadium is rarely present in ferrochromium in quantities warranting its determination. When it is desirable to determine it, this may be done, after reduction of the chromate and vanadate with ferrous sulfate, by oxidizing the vanadium alone by means of nitric acid. It is then titrated electrometrically with ferrous sulfate. This procedure has already been described elsewhere[1] by one of us.

Experimental

This method has been tested experimentally against pure potassium dichromate and mixtures of dichromate and finely powdered pig iron in which an exactly similar procedure as to fusion and solution was followed. The results are given in the table. In each case 1.9802 g. of potassium dichromate were used and one-tenth of this amount was titrated. The pig iron contained 0.04 per cent of chromium, for which correction was made.

ANALYSIS OF DICHROMATE ALONE WITH PIG IRON

Sample	Amount Pig Iron Gram	Fused with Na_2O_2 and Na_2CO_3	Chromium Present Gram	Chromium Found Gram	
				Gram	Gram
1	None	Not fused	0.7000	0.7002	0.7005
2	None	Fused	0.7000	0.7002	....
3	0.25	Fused	0.7000	0.7003	0.7008

This method was checked by oxidizing with ammonium persulfate. A portion of the third solution was treated with 25 cc. of sulfuric acid of sp. gr. 1.58, and diluted to 300 cc. After heating to boiling, 10 cc. of silver nitrate solution and 20 cc. of ammonium persulfate solution were added. After boiling 10 to 15 min., 5 cc. of dilute hydrochloric acid were added and the boiling was continued 5 min. Boiling with silver nitrate and ammonium persulfate served to oxidize all of the chromium and manganese, and boiling with hydrochloric acid decomposed the permanganic acid. After cooling and titrating, 0.7001 g. of chromium was found.

The procedure was next applied directly to a sample of ferrochromium. After preparing the solution for titration after the fusion with sodium peroxide, 100-cc. portions were reduced with an excess of ferrous sulfate and titrated with 0.1 *N* permanganate, correcting the titration with a carefully determined blank. The percentages of chromium found in this way were 63.43 and 63.65. Other portions of the solution titrated electrometrically with ferrous sulfate gave 63.48 and 63.48 per cent. One portion was boiled for 5 min. with 5 cc. of 1:3 hydrochloric acid, and on electrometric titration with ferrous sulfate after cooling gave 63.43 per cent. A portion was treated with an additional quantity of sulfuric acid and oxidized with silver nitrate and ammonium persulfate. The permanganic acid was destroyed with hydrochloric acid, and the solution was cooled and titrated electrometrically with ferrous sulfate. The value found was 63.46 per cent.

In all of this work where dependence was placed on the oxidation of the chromium by sodium peroxide, a portion of the solution was analyzed as soon as it had been made up to volume. This was found necessary owing to the

---

[1] Received April 28, 1921.

[2] This Journal, **8** (1916), 719.

[3] *Ibid.*, **13** (1921), 939.

[4] *Ibid.*, **9** (1917), 780.

[1] This Journal, **11** (1919), 632.

tendency of such solutions to show a lowered oxidizing capacity after standing. It occurred to the writers that this might be due to a slow reaction with traces of hydrogen peroxide which had not been decomposed by boiling the alkaline solution. To test this point, the solution obtained by dissolving the fused mass from a sample of ferrochromium was boiled 30 min., made up to volume, and on analysis found to contain 63.42 per cent chromium. After 4 days the apparent percentage of chromium was 62.10 and 62.20. A solution of another fusion was boiled 2 hrs. before acidification. The analysis of the freshly prepared solution gave 63.53 per cent chromium. After 4 days the apparent percentage of chromium was 63.05 and 63.15 per cent. It is thus clear that even boiling 2 hrs. does not give a stable solution.

SUMMARY

In this paper a method has been described for determining chromium in ferrochromium in which the chromate produced by oxidizing either with sodium peroxide or with silver nitrate and ammonium persulfate is titrated with ferrous sulfate, using an electrometric end-point. The procedure described has been in use in this laboratory for several years.

The Use of Perchloric Acid as an Aid to Digestion in the Kjeldahl Nitrogen Determination[1]

By **Brainerd Mears and Robert E. Hussey**

THOMPSON CHEMICAL LABORATORY, WILLIAMS COLLEGE, WILLIAMSTOWN, MASSACHUSETTS

On observing the corrosive action of 60 per cent perchloric acid on organic matter at somewhat elevated temperatures, it was decided to carry out a series of experiments in which small quantities of this material were used as an aid to digestion in the Kjeldahl determination of nitrogen. It was feared that the combination of sulfuric acid, perchloric acid, and organic matter might lead to serious explosions, but after running over 500 determinations with varying additions of perchloric acid without an explosion and at most with only a rapid deflagration, it was determined that this reaction was not particularly dangerous. In most instances, however, the perchloric acid, sulfuric acid, and other materials were mixed cold. It was also feared that there might be considerable loss of nitrogen due to the volatilization or decomposition of the ammonium perchlorate which might be formed at the elevated temperatures, or that other interfering factors might develop.

EXPERIMENTAL DETAILS

A series of preliminary experiments proved that the addition of copper sulfate was beneficial, that it was impracticable to attempt to regulate the temperature of the digestion, and that most of the ammonia remained in the digestion flask. Accordingly, with a view to obtaining comparable data on the use of the perchloric acid, the following experiments were carried out. One-gram samples of casein, tankage, egg albumin, gelatin, and dried blood, and about 10-g. samples of urine and milk were treated with 25 cc. of concentrated sulfuric acid and 1 g. of copper sulfate. Several determinations were run by the official Gunning method, slightly modified,[2] as a check on the nitrogen content of the material and to furnish an estimate of the time required for the complete digestion of the sample. At the same time, a series of determinations containing the same quantities of sulfuric acid and copper sulfate but with increasing amounts of the perchloric acid was carried on. Blank checks were run on the reagents in each instance, the average of which showed a nitrogen content of 0.0027 per cent. In some instances, because of the lack of uniformity or low nitrogen content of the samples, the accuracy of the determinations might have been increased if larger samples had been employed, but it was considered advisable to keep the quantity of the sample constant to assist in drawing conclusions from the results obtained. The 1 g. of copper sulfate employed was probably more than was required; but inasmuch as many of the experiments were run with this quantity and no harmful effects were observed from its presence, the same quantity was employed in all the determinations. The study of the Kjeldahl method by the Association of Official Agricultural Chemists,[1] partly substantiates these conclusions. Table I summarizes the results obtained.

TABLE I

METHOD	No. of Determinations	Time of Digestion Hrs.	Time of Digestion Min.	Per cent Nitrogen Max.	Per cent Nitrogen Min.	Per cent Nitrogen Av.
MILK						
Kjeldahl	3	4	30	0.70	0.69	0.70
Modified $HClO_4$:						
1 cc.	1	2	30	0.68	0.68	0.68
2 cc.	3	1	30	0.69	0.67	0.68
3 cc.	4		25	0.69	0.69	0.69
4 cc.	2		25	0.69	0.67	0.68
5 cc.	1		10	0.64	0.64	0.64
URINE						
Kjeldahl	4	1	45	1.02	0.92	0.99
Modified $HClO_4$:						
0.5 cc.	4		20	0.99	0.96	0.98
1 cc.	6		20	0.89	0.84	0.87
2 cc.	6		20	0.81	0.73	0.77
3 cc.	2		20	0.74	0.67	0.70
4 cc.	2		20	0.66	0.61	0.64
5 cc.	2		20	0.66	0.56	0.61
CASEIN						
Kjeldahl	7	4		12.44	12.14	12.29
Modified $HClO_4$:						
1 cc.	4	1	15	12.31	12.17	12.22
2 cc	12		20	12.40	12.14	12.31
3 cc.	2		20	12.26	11.45	11.85
4 cc.	2		20	11.41	10.64	11.03
5 cc.	2		20	10.81	10.55	10.68
TANKAGE						
Kjeldahl	8	3		8.06	7.55	7.76
Modified $HClO_4$:						
1 cc.	2	1	30	7.80	7.73	7.78
2 cc.	5		20	7.89	7.54	7.73
3 cc.	2		20	7.55	6.32	6.93
4 cc.	2		20	6.70	5.95	6.34
5 cc.	2		20	6.30	6.20	6.25
ALBUMIN						
Kjeldahl	11	2	30	12.03	11.81	11.89
Modified $HClO_4$:						
1 cc.	2	1	15	11.93	11.86	11.89
2 cc.	6		20	12.12	11.90	12.02
3 cc.	2		20	11.64	11.00	11.32
4 cc.	2		20	9.85	9.32	9.59
5 cc.	2		20	9.44	9.21	9.33
GELATIN						
Kjeldahl	7	3		14.38	14.34	14.36
Modified $HClO_4$:						
1 cc.	2	1	15	14.38	14.34	14.36
2 cc.	3		20	14.43	14.36	14.38
3 cc.	2		20	12.75	10.77	11.76
4 cc.	2		20	10.96	9.74	10.35
5 cc.	2		20	11.08	9.43	10.25
DRIED BLOOD						
Kjeldahl	7	4	30	13.14	13.09	13.11
Modified $HClO_4$:						
1 cc.	3	1	30	13.09	13.06	13.08
2 cc.	3		20	13.11	13.10	13.11
3 cc.	1		20	11.88	11.88	11.88
4 cc.	1		15	11.92	11.92	11.92
5 cc.	2		15	11.93	11.93	11.93

The curves which follow were obtained by employing the above data and plotting the percentage of nitrogen against the quantities of perchloric acid used.

DISCUSSION OF RESULTS

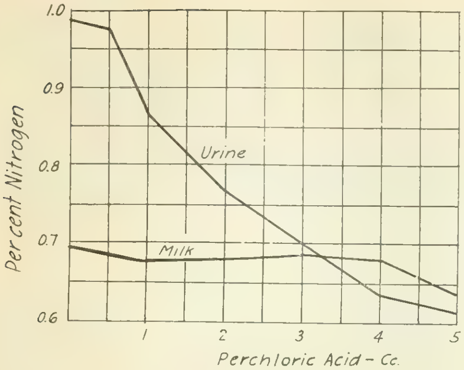
It is to be observed that, with the constant condition of a 1-g. sample, plus 1 g. of copper sulfate and 25 cc. of con-

---

[1] Received June 3, 1921.

[2] A. O. A. C., "Methods of Analysis," **1920**, 7.

[1] Vol. **4**, 367.



centrated sulfuric acid, the per cent of nitrogen obtained remains fairly constant, with a marked decrease in the time required for the digestion, up to the addition of 2 cc. of the perchloric acid to the 1 g. of solid material. Beyond that point there is a rapid and increasing loss of nitrogen, as shown by the slope of the curves. The plotted results of the milk and urine show curves which differ somewhat from the solid samples, but here the presence of water and the varying quantity of solid material, although they change conditions to some extent, apparently point to relatively the same conclusions.

Confining our observations to the solids analyzed, we conclude that 2 cc. of 60 per cent perchloric acid per gram of solid material furnishes the most rapid digestion and gives results which are influenced little, if at all, by the presence of this acid. It was also observed that the best perchloric acid results were obtained from determinations which cleared in not less than 3 min. or more than 7 min. from the time of lighting the gas under the digestion flask, and which were heated for 15 min. after clearing. The 2 cc. of perchloric acid and the 1-g. sample usually conformed to these requirements. It would seem then that sufficient perchloric acid must be present to decompose the organic material, but that the presence of an excess causes a loss of nitrogen.

Experiments performed on 2-g. samples of the solid material with 4 cc. of perchloric acid gave comparable results. Attempts were also made to add an excess of perchloric acid, digest and clear the sample, and neutralize the undesired excess of acid by the addition of pure cane sugar. The results were of fair accuracy, but flaming and other attendant difficulties caused the procedure to be abandoned. The use of perchloric acid, diluted with water, and the use of smaller quantities of sulfuric acid, even as little as 10 cc. in some instances, gave accurate results; but in many cases there was a considerable loss of nitrogen.

Experiments were also carried on by adding perchloric acid in varying quantities in the determination of nitrogen in nitrates by the Gunning method. While results of fair accuracy were obtained, little time was saved because of the time required for the cooling of the digestions before the addition of the acid, and it was therefore concluded that little was to be gained by the application of the procedure to this class of substances, except perhaps where the substances employed were exceedingly difficult to digest.

APPLICATION OF METHOD TO OTHER SUBSTANCES

In order to apply the method to a greater variety of substances, samples of sheep manure, cocoa shells, castor pumace, rapeseed meal, and hoof meal of known nitrogen content were obtained from a most reliable source. Many of the samples were reported to be difficult to digest and in some instances had lost moisture on storage. Some samples were not uniform in composition.

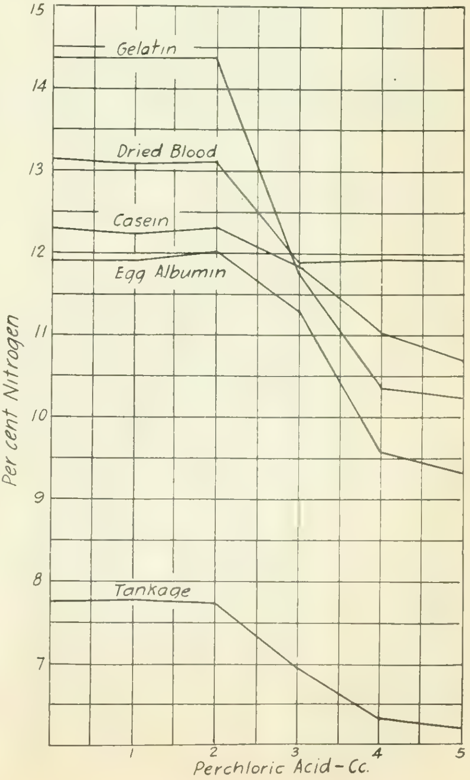
By the use of 1-g. samples with 25 cc. of concentrated sulfuric acid, 1 g. of copper sulfate, and 2 cc. of 60 per cent perchloric acid (unless the trial run showed by its rate of clearing a need of more or less of this acid) the results recorded in Table II were obtained. It seems that they may be considered a fair check when obtained by two independent investigators working in different laboratories at different times.

TABLE II

(Time of digestion, 20 min.)

SUBSTANCE	No. of Determinations	Per cent Nitrogen Maximum	Per cent Nitrogen Minimum	Per cent Nitrogen Average	Per cent Nitrogen Stated to Be Present in Sample
Sheep manure	6	1.54	1.41	1.48	1.48
Cocoa shells[1]	5	2.43	2.41	2.42	2.22
Castor pomace	5	5.83	5.67	5.72	5.80
Castor pomace[2]	3	3.54	3.37	3.45	3.33
Rapeseed meal[2]	3	5.69	5.67	5.68	5.74
Garbage tankage	5	8.44	8.41	8.42	8.58
Cattle manure	1	2.17	1.92	2.09	1.88
Tankage (6–30)[1]	3	4.86	4.73	4.81	4.98
Tankage (10–20)	3	7.67	7.50	7.61	7.62
Cottonseed meal (dark)	3	6.59	6.48	6.54	6.69
Hoof meal[1]	3	15.35	15.27	15.32	15.23

[1] Corrected for moisture.
[2] 3 cc. of perchloric acid used.



Summary

From the above results it is concluded that the use of small quantities of 60 per cent perchloric acid considerably shortens the time of digestion in a Kjeldahl determination, without appreciably affecting the accuracy of the results, in the class of substances investigated, provided that the quantity of the acid added does not cause the digestion to clear in less than 3 min. or fail to clear in 7 min.; that 1-g. samples treated with 25 cc. of concentrated sulfuric acid plus 1 g. of copper sulfate with 2 cc. of perchloric acid usually fulfil these requirements; and that all samples should be heated at least 15 min. after clearing.

LABORATORY AND PLANT

Constant Temperature Rooms[1,2]

By E. G. Hastings

Laboratories of the Department of Agricultural Bacteriology, University of Wisconsin, Madison, Wisconsin

Until comparatively recently the constant temperature room was considered an essential part of the equipment of a bacteriological laboratory, but not of a chemical laboratory. With the widening interest and activity in biochemistry, the chemist has come to consider such a room as a vital portion of his equipment. In many, indeed in most cases, a large amount of money has been spent in providing complicated heating devices and in insulating the rooms.

The incubator equipment of the Department of Agricultural Bacteriology of the University of Wisconsin has been gradually developed, as the need for increased space has arisen. The need has been met with limited resources. It is thought that a brief presentation of the essential portions of the equipment may prove of interest to others who wish to extend their facilities in this direction.

The laboratories are provided with four incubator rooms of varying sizes. In each instance a room originally used as a store room and opening off a laboratory has been adapted for incubator purposes. No money has been spent in insulating the walls, the lath and plaster of the original building forming the only insulation. False ceilings have been installed in order to diminish the height of the rooms and to avoid heating space that was inaccessible. Two of the rooms are provided with double doors, one swinging into the room, the other outward. The other rooms have single, light wood doors.

Heating Devices

Three of the rooms are heated with gas. A bottomless box of galvanized iron (Fig. 1) about 16 in. × 14 in. × 17 in. high has been constructed with a door on one side. A row of holes near the bottom of the box permits the entrance of air. A rectangular galvanized iron pipe 12 by 6.5 in. in section is carried from the side of the box across one side of the room and then upward to the ceiling, where it joins a 6-in. round pipe which enters one of the ventilating flues of the building. A damper is installed in the round pipe to prevent the too rapid passage of air through the pipe and the consequent excessive loss of heat.

Gas is piped to the box and on the end of the supply pipe a rose-top Bunsen burner is connected with threaded joints. In the line of the supply pipe a Roux bimetallic regulator with a horseshoe shaped bar is installed with a bypass provided with a stopcock. The stopcock is for the purpose of allowing a small amount of gas to pass to the burner in case the regulator should not function. As far as our experience goes it is not an essential part of the equipment. As the heated gases pass through the pipe they are robbed of their heat by the extensive radiating surface of the pipe. The maximum use of the gas is thus obtained. One room has a content of 430 cu. ft. The radiating surface of the box and pipe is approximately 52 sq. ft. The room is heated to a temperature of 35° C. by one burner. The records presented in Fig. 2 show the temperature variations of the room during a period when it was opened only a few times each day. The maximum temperature variation of the rooms surrounding the room in question during the period covered by the records was 15° C.

The fire hazard is nil, since the two possible sources of danger are excluded. Danger from a burner that strikes back is avoided by using only threaded joints and by not allowing the supply pipe to come in contact with wood for 3 or 4 ft. from the burner. The danger from an extinguished burner is avoided by the passage of the gas into the ventilating flue. One of the rooms is so situated that access to a ventilating flue could not be gained. The gases from the heating pipe are discharged into a hall, the cubical content of which is so great that an explosive mixture would not be obtained, unless the gas was allowed to escape for many hours. The absence of danger from fire was well shown by an incident of recent occurrence. One of the rooms is provided with two burners. During the summer one is sufficient to maintain the temperature at the desired point, but in the winter two are needed. The gas was turned off the building for the purpose of making repairs. When it was turned on again, one of the burners was lighted, but not the other, which was discharging gas. This unlighted burner was not discovered for 48 hrs. The gas from it did not catch fire, although the two burners were in the same box and not over 4 in. apart. The current of air through the box was sufficient to prevent the ignition of the gas and to carry it away so rapidly as to prevent an explosive mixture being reached in the box. No odor of gas could be noted in the room. The unlighted condition of the one burner was detected by the lowered temperature of the room.

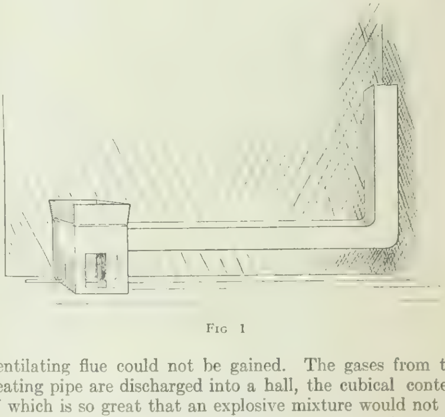


Fig 1

---

[1] Received May 11, 1921.

[2] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

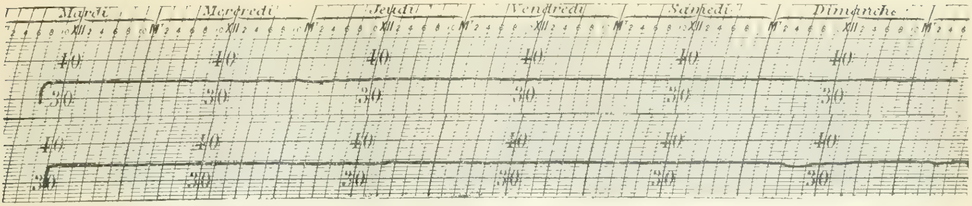


Fig 2—Thermograph Records of a Noninsulated Constant Temperature Room Heated with Gas Controlled by a Roux Bimetallic Regulator

Avoidance of Stratification

One trouble encountered in incubator rooms is the stratification of the air. In the rooms heated by the method described, this is almost completely overcome by allowing air to enter the room at the top of the door. This cool air lowers the temperature at the top of the room, while the constant removal of the cold air at the floor through the heating device tends to prevent low temperatures near the floor. The temperature is sufficiently uniform so that cultures of *B. tuberculosis* grow well at any level in the incubator. The importance of this movement of air in equalizing temperature was not fully realized until another room was equipped with a different heating device.

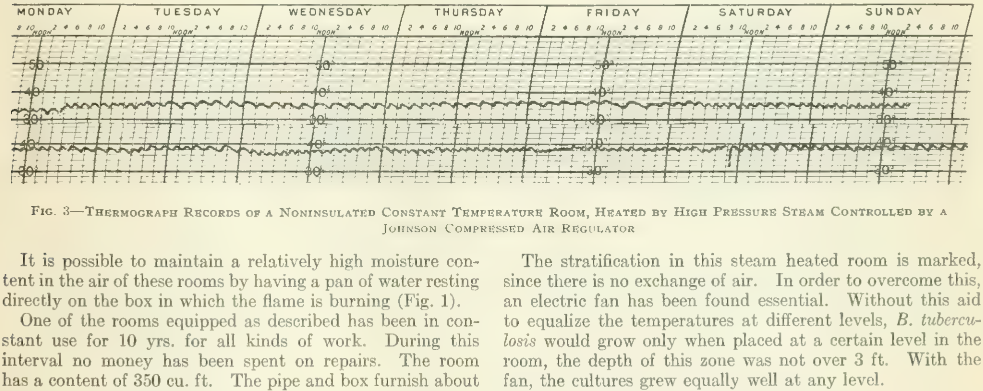


Fig. 3—Thermograph Records of a Noninsulated Constant Temperature Room, Heated by High Pressure Steam Controlled by a Johnson Compressed Air Regulator

It is possible to maintain a relatively high moisture content in the air of these rooms by having a pan of water resting directly on the box in which the flame is burning (Fig. 1).

One of the rooms equipped as described has been in constant use for 10 yrs. for all kinds of work. During this interval no money has been spent on repairs. The room has a content of 350 cu. ft. The pipe and box furnish about 30 sq. ft. of radiating surface.

The lack of insulation of the rooms has caused the use of more gas than would have been necessary with insulation. The interest charges and depreciation on insulated rooms would go far to offset the additional expense for gas, and probably would more than equal this charge. The amount of heat that one or two burners will supply is not sufficient to maintain the non-insulated rooms at the temperature desired if the temperature of that part of the building surrounding the rooms varies too widely.

During the past year a steam-heated room has been in use. The room is a basement one with concrete floor, one outside wall with window equipped with an inside shutter of wood. A single door is provided. The radiator that was in the room was connected to the high pressure steam pipes on which a pressure of 20 lbs. is carried throughout the year. The regulation is by means of a Johnson compressed air regulator, such as is used in many of the university buildings. By these regulators the steam is turned off and on; thus the heat supplied varies from zero to the maximum capacity of the radiator. The temperature of the room varies by such an extent as is necessary to cause the regulating device to function. The thermograph record of such a room will not present a straight line, but a line with uniform variations when the regulator is operating properly. In Fig. 3 thermograph records of this room are presented. It is to be noted that the temperature of this room has varied regularly over a space of about 2° C. During the past few months it has been used most successfully for the growing of *B. tuberculosis* in connection with the preparation of tuberculin. The regular variations in temperature noted in this room are of no importance in most lines of work.

There is a large reserve of heat, and the room has been kept at the desired temperature irrespective of variations in temperature of the rooms surrounding it, or out of doors.

The stratification in this steam heated room is marked, since there is no exchange of air. In order to overcome this, an electric fan has been found essential. Without this aid to equalize the temperatures at different levels, *B. tuberculosis* would grow only when placed at a certain level in the room, the depth of this zone was not over 3 ft. With the fan, the cultures grew equally well at any level.

The total expense connected with the adaptation of these rooms for incubating purposes, including regulators and shelving, has been less than $800. The total content of the four rooms is 2200 cu. ft.

One of the rooms is provided with racks which carry small metal drawers with bottoms of wire screen. These drawers are assigned to individual students, and may be carried to the working desk. The other rooms are provided with shelves of wire mesh supported on a frame work.

The plant of the Union Dye and Chemical Company at Kingsport, Tenn., was sold at auction on September 19, 1921, in accordance with the decree of the Chancery Court of Kingsport, arising from a suit against the company brought by the Equitable Trust Company of New York and Lyman Roades. The plant went into the hands of the receiver about January 1, 1921. The property, machinery, equipment, a tract of land and real estate of the corporation were sold for $185,000 and chemicals on hand for $15,000, making a total of $200,000. The plant was bought by a New York attorney who is said to have been acting for a corporation which expects to operate it. Prior to the war the Union Dye plant was used for the manufacture of dyes, but was taken over by the Government for the manufacture of high explosives. At the close of the war the plant became inactive and several buildings are in need of immediate repair.

Flask Calibrating and Marking Device[1]

By Guilford L. Spencer

The Cuban-American Sugar Co., Tinguaro, Cuba

This device was originally intended only for marking precision flasks. It may be used, however, in combination with a calibrating buret in judging the accuracy of the marking of such flasks. It locates the position of the meniscus with greater accuracy than is possible by the eye, with customary aids.

As is evident in the drawing, the device is a means of bringing a pair of electrodes into contact with acidulated water at the center of the meniscus, in the neck of the flask, indicating the point of contact, and marking the neck with a ring at this level.

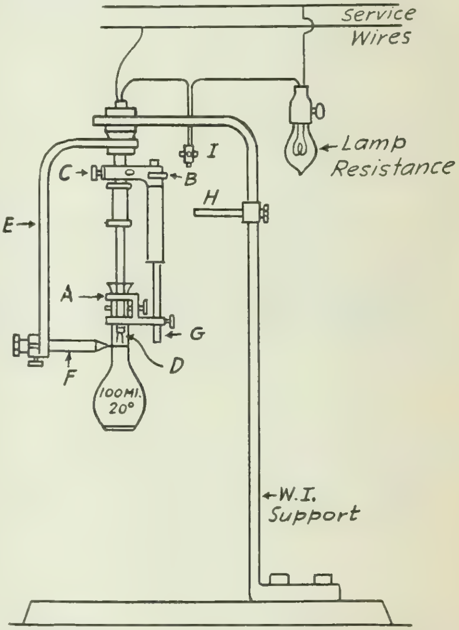
The electrodes are connected in series with an incandescent lamp and the service wires. If desired, a cell containing dilute sulfuric acid, into which dip platinum wires, also in series with the lamp, may be used in addition to the signal (described later) for indicating the contact of the electrodes with the liquid in the flask. A galvanometer could be used for this purpose, but these devices have not been found necessary. The audible and visual signals of the contact of the electrodes at the meniscus are clear and within the accuracy of the calibrating buret and the practical applications of the flasks.

The liquid used in calibrating is distilled water, containing about 1 cc. of sulfuric acid per liter. The usual precautions of expelling the air from the dilute acid and avoiding vibration and temperature fluctuations are observed. The neck of the flask is varnished or waxed in a wide band at the probable location of the mark; the flask is clamped in its holder; the desired volume of acidulated water is measured into it with the calibrating buret. The holder is next slipped over the micrometer post, with the guide pin in the groove, and the flask is raised nearly to contact of the electrodes with the liquid; and the holder is clamped to the post and is centered by means of the three screws.

Previous to placing a flask in the apparatus, the graving needle is so adjusted that its point falls at the bottom of the central electrode and it is then withdrawn. A lock nut is provided for making this adjustment, which is semi-permanent.

Having centered the flask, the switch is closed, and the micrometer head is turned little by little, lifting the flask until the central electrode, which is slightly higher than the other, touches the liquid. At the instant of contact, there is a distinct sound made by the evolution of gases, and this or the appearance of gas shows that the contact has been made. The wattage of the incandescent lamp determines the distinctness of the signal. The switch is now opened. Experience has shown that with rapid work, and before the gas and heat evolved appreciably affect the liquid, three or four contact points can be located within the limits of accuracy of the calibrating buret, and guided by the noise only, or in other words, with the operator blindfolded. The graver is now pushed till nearly in contact with the neck of the flask and then, by means of the fine adjusting screw, to full contact. A spring and follower press against the graving needle. The spring and follower in the graver-holder, bearing on the graver, provide against the effects of slight distortion of the neck, or failure to exactly center the flask. The sweep is revolved and the graver cuts a ring in the varnish or wax, and the glass is ready for etching.

The micrometer may be made with standard taps and dies (S. A. E.) 24 threads per in. This corresponds nearly to 1.058 mm. pitch or vertical travel of the post per complete revolution of the head. Since the micrometer head is sensitive to less than one-twentieth revolution, the instrument is sensitive to less than 0.0529 mm. vertical travel of the post. Assuming the marking of a Bates' 100-cc. flask of 12 mm. internal neck diameter: Area = 113.1 sq. mm. and 113.1 × 0.0529 = 5.98 cu. mm. or 0.006 cc. It is possible to graduate a liter flask of 20 mm. internal neck diameter to 0.02 cc. This is well within the limits of the accuracy of the calibrating buret. A smaller post having 28 threads per in. (S. A. E.) or a metric post could be used if desired.



A—Flask-clamp
B—Micrometer head and post
C—Flask centering-screws
D—Platinum electrodes
E—Sweep
F—Graving tool
G—Lower end of micrometer post
H—Adjustable plate for hand rest
I—Switch

A pointed screw was used, in graving, in the original model of the instrument. It was noted in marking single-graduation flasks that the errors fell on either side of the correct number, but in two graduation flasks, the errors of the upper marking usually fell on one side. This was possibly due to a difference of neck diameter and a slight eccentricity of the point. The sliding graver was devised to assure a correct average.

The flasks listed below were graduated with the original model, using the screw-graver and a centering flask-clamp. The first two lots of flasks were checked against "double-checked" weights on a chainomatic balance and the others against calibrating burets, certified by the Bureau of Standards:

---

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

50/55 Cc.		50/55 Cc.		100 Cc.	
50.014	0.014	49.993	0.007	99.776	0.024
54.981	0.019	54.979	0.021	99.987	0.013
				100.026	0.026
50.019	0.019	49.974	0.026	99.990	0.010
54.972	0.028	54.969	0.031	100.012	0.012
				100.004	0.004
50.029	0.029	50.016	0.016		
54.980	0.020	54.967	0.033		

The above 100-cc. flasks were chosen at random from forty-eight consecutively graduated, and checked against weights. One out of every six of the remaining flasks was tested against the calibrating buret. The extreme range was 99.98 to 100.02 cc. Many of these flasks have been rechecked when issued to the factory laboratories and appear in the foregoing lists.

FLASKS CHECKED WHEN ISSUED

50/55 Cc.	50/55 Cc.	100 Cc.	300 Cc.	500 Cc.[1]
50.00	50.01	100.01	299.98	499.97
54.99	55.00	100.00	300.02	499.95
		99.98	300.00	
50.02	49.99	100.00	300.02	
55.00	54.99	99.99	299.99	
		99.99	300.02	
50.00	49.99	99.97	299.98	
55.00	55.00	100.01	299.97	
		100.00	300.02	
50.02	49.99	100.01	299.97	
54.99	54.99	99.98	299.99	
		99.99	300.01	
50.00	50.00	99.99	300.02	
55.00	55.02	100.00		
		99.99		
50.00	50.00	100.02		
55.00	55.01	100.00		
		99.99		
50.00	50.01			
55.00	54.99			

A similar method of marking has been considered by the author but has not been tried out. In this a very fine capillary tube of glass replaces the electrodes and tinted water the diluted acid. At the instant of contact of the capillary tube and the water, the latter shows clearly in the tube. The author found a description of this method of measurement in an old edition of Mohr's "Titrirmethode," after he had used it several years.[1]

This method of measurement may be applied in determining the specific gravity of viscous material that cannot be tested with the customary appliances, using instead a tube or cylinder. For example, molasses, freed of air by suction, is weighed in a tube of 15 mm. internal diameter that has been calibrated with a modification of the marking device. Water is measured upon the molasses from a closely divided buret until contact with the electrode is made. The calculations are obvious. The accuracy of measurement in this case in so far as regards the electrode device, is approximately 0.01 cc. The electrode would be in fixed position. This method could be used with larger vessels, *e. g.*, of 50 mm. diameter, with accuracy of the third decimal place.

The work of marking and calibrating the flasks listed in this paper is by Mr. Joseph B. Harris, Control Chemist and Assistant Superintendent, Cardenas (Cuba) Refinery.

---

[1] Five measurements with 100-cc. calibrating buret in calibrating and in checking.

[1] Spencer, "Handbook for Chemists of Beet-Sugar Houses," 1897.

ADDRESSES AND CONTRIBUTED ARTICLES

The Forests of the United States as a Source of Liquid Fuel Supply[2]

By **Ralph C. Hawley**

YALE UNIVERSITY, NEW HAVEN, CONNECTICUT

The purpose of this paper is to present a concise statement showing the amount of wood available for conversion into liquid fuel which can be produced annually on the forest lands of the United States (Alaska and insular possessions excluded).

The forested area of the United States is as follows:

TABLE I—AREA AND GROWTH OF THE FORESTS OF THE UNITED STATES[1]

AREA FORESTED Acres	CHARACTER	PRESENT GROWTH Cu. Ft.	POSSIBLE GROWTH Cu. Ft.
245,000,000	Second growth forests	5,995,000,000	14,700,000,000
81,000,000	Waste land on which nothing is growing or likely to grow without reforestation	Nothing	4,860,000,000
137,000,000	Virgin forests	Nothing	8,220,000,000
463,000,000		5,995,000,000	27,780,000,000

[1] All figures in this table are taken from "Timber Depletion, Lumber Prices, Lumber Exports and Concentration of Timber Ownership," Report on Senate Resolution **311** by The Forest Service, U. S. Department of Agriculture.

To-day the annual growth of wood is approximately six billion cubic feet. The possible growth, provided the lands are properly restocked after cutting, and protected, is conservatively estimated at twenty-seven and three-quarters billion cubic feet per year.

Not all of this annual growth would be available for manufacture into liquid fuel. Lumber and numerous other forest products must be provided for.

Each year approximately twenty-six billion cubic feet of wood (far in excess of the present growth and taken principally from the accumulation of virgin timber) are removed from the forests, distributed as shown in Table II.

TABLE II—AMOUNT OF WOOD REMOVED ANNUALLY FROM THE FORESTS OF THE UNITED STATES[1]

CUT	Equivalent in Standing Timber, Cu. Ft.
Lumber	8,913,300,000
Fuelwood	10,450,000,000
Other products	4,955,615,000
Destroyed by fire, insects and fungi	1,730,000,000
TOTAL	26,048,915,000

[1] All figures in this table are taken from "Timber Depletion, Lumber Prices, Lumber Exports and Concentration of Timber Ownership," Report on Senate Resolution **311** by The Forest Service, U. S. Department of Agriculture.

Out of this total cut, at least 4,800,000,000 cubic feet cut for lumber are lost through waste in the woods and at the mills. Adding to this the 1,730,000,000 cubic feet destroyed by fire, insects, and fungi gives a total of 6,530,000,000 cubic feet of wood annually wasted which should be available for liquid fuel, without encroaching upon the supply needed for other purposes. Furthermore, the possible annual growth (27,750,000,000 cubic feet) exceeds the annual requirements (26,000,000,000 cubic feet) by 1,750,000,000 cubic feet, furnishing an additional 1,750,000,000 cubic feet for liquid fuel.

TABLE III—ESTIMATE OF AMOUNT OF WOOD FOR LIQUID FUEL WHICH COULD BE SECURED FROM FORESTS OF THE UNITED STATES WITHOUT ENCROACHMENT UPON SUPPLY OF OTHER FOREST PRODUCTS

		Cu. Ft.
Waste in the woods and at the mills		4,800,000,000
Losses from fire, insects and fungi	(taken out in thinnings)	1,730,000,000
Excess of possible growth over annual cut	(taken out in thinnings)	1,750,000,000
Increased growth due to more intensive crop management	(taken out in thinnings)	2,750,000,000
TOTAL		11,030,000,000

Finally, the increased growth which will follow intensive forest crop management, particularly the removal of small wood in thinnings, should amount to not less than 10 per cent of the possible growth, or 2,750,000,000 cubic feet.

---

[2] Presented before the Section of Cellulose Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

This gives a total of 11,000,000,000 cubic feet, as summarized in Table III. How much liquid fuel will this 11 billion cubic feet of wood produce?

In making the calculation a cubic foot of wood is taken as weighing 30 pounds and a ton of wood as yielding 15 gallons of alcohol. On this basis the 11,000,000,000 cubic feet of wood will furnish an annual output of 2,475,000,000 gallons of alcohol or 33 per cent of the total amount of alcohol needed to replace the present output of gasoline.

The cost of the raw wood laid down at the manufacturing plant is estimated to average 25 cents per gallon of alcohol produced by present methods, although where the proper region and species are chosen this figure may be reduced to 7 cents a gallon. (See Examples 2 and 3.) It remains for the chemists to develop improved methods of utilizing the cellulose more completely, thereby increasing the output of liquid fuel secured from a ton of wood.

Professional foresters may be expected to coöperate fully with the chemists in their efforts to utilize wood as liquid fuel for at least two reasons: First, because utilization of waste in the woods and at the mills will clear the forest of material now unsalable which is often a dangerous fire and insect hazard, and second, because the opportunity to dispose of small trees in thinnings will make more intensive forestry possible, and this in turn will increase the quality and quantity of forest crop production.

It is realized that the utilization of wood as liquid fuel on a large scale is not likely to come for a decade or more. In order to have available when needed the largest possible annual supplies of wood, forested areas must without delay be protected, scientifically cut, and completely restocked. For this reason the support of your organization is desired for measures looking to better care of the nation's forest resource.

EXAMPLES

Three examples are added to show the results possible in different sections of the country in growing forest crops for liquid fuel. The first is for hardwoods in Connecticut, which are of relatively slow growth. The other two examples are given to indicate the possibilities in the South and the West with rapid-growing conifers.

EXAMPLE 1. *Hardwoods in Connecticut*—The forests of Connecticut are of mixed hardwood character, the principal species being oak, hickory, birch, maple, and ash. They cover an area of 1,500,000 acres and are capable of producing not less than 67,500,000 cubic feet a year. One-third of the growth, or 22,500,000 cubic feet, could be removed each year in thinnings and converted into alcohol. At present this class of material is not generally utilized.

Connecticut hardwoods are estimated to average 40 pounds per cubic foot and to yield 10 gallons of alcohol per ton of wood. The 22,500,000 cubic feet on this basis will yield annually 4,500,000 gallons of alcohol.

The cost of the raw wood laid down at the plant is estimated to be 28 cents per gallon of alcohol secured.

EXAMPLE 2. *Shortleaf Pine in Virginia*—Shortleaf pine is one of the southern pines and has a commercial range of more than 150,000,000 acres throughout the southern states. It would be an excellent tree to grow as a crop for conversion entirely into liquid fuel.

A 25-year rotation[1] shows a wood production of 208 cubic feet per acre per year. Allowing a weight of 30 pounds per cubic foot of wood and 20 gallons of alcohol per ton of wood the annual yield of alcohol per acre would be over 62 gallons.

The cost of the raw wood laid down at the plant should not exceed 7 cents per gallon of alcohol secured.

For an annual production of one million gallons of alcohol to be maintained indefinitely 16,129 acres of land would be required. Approximately 645 acres would be cut clear each year. Each acre when cut clear would yield 5220 cubic feet or 1566 gallons of alcohol.

EXAMPLE 3. *Douglas Fir in Western Oregon and Washington*—West of the Cascade Mountains in Oregon and Washington, Douglas fir is the chief commercial species and is used largely for lumber. Approximately 15,400,000 acres west of the Cascades are nonagricultural lands suitable for growing Douglas fir.

On an 80-year[1] rotation for lumber as the chief product, the annual production of these lands is estimated at over 2,000,000,000 cubic feet, of which 800,000,000 cubic feet could be removed annually in thinnings.

Allowing 30 pounds per cubic foot of wood and 20 gallons of alcohol per ton of wood, the annual production of alcohol from wood taken out in thinnings totals 240,000,000 gallons, or 3.2 per cent of the alcohol needed to replace the present output of gasoline.

If it is desired to grow Douglas fir as a crop for complete utilization as liquid fuel, a 40-year rotation should be used.

On the better-grade lands, a production of 275 cubic feet of wood could be produced per acre per year, or 82.5 gallons of alcohol.

The cost of the raw wood laid down at the plant should not exceed 9 cents per gallon of alcohol secured.

For an annual production of one million gallons of alcohol to be maintained indefinitely 12,121 acres of land would be required. Approximately 303 acres would be cut clear each year. Each acre when cut clear would yield 11,000 cubic feet or 3,300 gallons of alcohol.

---

[1] These figures are taken from United States Department of Agriculture, *Bulletin* 308 by W. R. Mattoon, "Shortleaf Pine: Importance and Management."

[1] See "The Productive Capacity of the Douglas Fir Lands," by T. T. Munger, University of California, *Journal of Agriculture*, November **1916**, 92.

Industrial and Technical Photography

During the last few years photography has developed as an important factor in industry, commerce, and science, and a number of large concerns have established permanent photographic departments as an aid to better efficiency in administration, engineering, research, buying, selling, advertising, education, coöperation, etc.

Mr. John H. Graff, of Brown Co., Berlin, N. H., is planning to make a survey of the use of industrial and technical photography. With this end in view, he is asking those interested in the subject to send him samples of different types of photographs used; a short statement of how and why photography is being used, as in field, office, plant or research; information as to how far an outside photographer is employed; or, if the users have photographic departments of their own, a history of the development of the same. Methods of mounting, filing, and reference are important; also statements of the costs and upkeeps of the departments and their value and importance.

Would it be advisable to recruit help for photographic department from the photographic profession, or to develop employees for this work? Should our technical schools develop men as photographic engineers to meet the growing demand for practical, industrial photographers?

After this information is received, Mr. Graff plans to combine it in a complete history of the development and uses of industrial photography, to be published in a technical magazine. The more each one contributes to an article of this kind, the more valuable it becomes.

Mr. Graff is also making the following inquiries: Would a convention of the users of industrial and technical photography be of any value? If so, would you pledge your presence and support to a convention of this kind, and where would you suggest this to be held? If enough interest could be aroused, the plan would be to arrange a conference with an exhibition of all forms of technical and industrial photographs, and with lectures on different photographic subjects in relation to industry, science, research, and commerce.

Colors Developed by Cobalt Oxides[1,2]

H. J. Witteveen and **E. F. Farnau**

UNIVERSITY OF NORTH DAKOTA, GRAND FORKS, NORTH DAKOTA

The colors which cobalt oxides exhibit either as hydrous oxides or in sintered or fused masses with metallic oxides, borates, and silicates are so characteristic as to afford valuable individual tests in qualitative analysis, and so brilliant in some cases as to serve as pigments. Although these facts and applications have been known and applied for a long time (even the ancients having used cobalt blue as a pigment), no effort has been made to classify the color phenomena.

With the scattered data collected, it is the purpose of this paper to offer an hypothesis which will account for the apparently erratic color effects shown by the numerous oxides, alone, hydrated, or in physical or chemical combination with metallic oxides and fluxes.

HISTORY

The data which are here collected have been arranged according to composition and not chronologically. The name and formula of the substance are given, with methods of preparation and properties.

CoO—COBALTOUS OXIDE—Formed by heating Co_3O_4 in nitrogen. When heated in air it oxidizes to the black higher oxide. It is not oxidized at ordinary temperature even on long standing. It is soluble in warm concentrated potassium or sodium hydroxide solution, yielding a deep blue color.

Color: Light Brown[1] Formed by ignition of Co_3O_4 in carbon dioxide[2]
Color: Brown: Formed by reduction of Co_3O_4 with hydrogen.[3]
Density: 5.68;[4] 6.7.[5]

$Co(OH)_2$—COBALTOUS HYDROXIDE—Formed by the precipitation of cobaltous salts in absence of air with concentrated potassium hydroxide, yielding blue basic salts which go over through violet into a rose-red hydroxide (more rapidly when warmed).[6, 7]

Boiling cobaltous carbonate with potassium hydroxide solution forms a voluminous blue oxide, which turns violet and then yields a rose-red hydrate.[8,9]

It can also be formed by heating a solution of 10 g. of $CoCl_2.6H_2O$ in 60 cc. of water with 250 g. of potassium hydroxide under an atmosphere of illuminating gas; the cobaltous hydroxide dissolves, yielding a blue color. After 24 hrs. the precipitated crystals are washed with water.[10]

The alkaline solutions contain the cobaltous hydroxide as a colloid since it is not dialyzable and is precipitated on barium sulfate by shaking with the latter. This is true also of the blue alkaline solution in glycerol and also of the green solution obtained by oxidation with air.[11]

Hantzsch[12] found that the blue precipitate obtained at first when cobalt salts were precipitated by alkalies was cobalt salt. In the absence of the latter, *i. e.*, with excess of alkali, the blue changes quickly to the pink hydroxide.

In some experiments carried out at New York University, the authors have shown that the pink hydroxide may be changed to blue by allowing it to stand in contact with cobalt solutions.

MAGNESIUM COBALTITE—When magnesium oxide is heated with cobalt nitrate it takes on a pale rose-red color. Minerals which contain magnesium also take on a rose-red color, upon heating with cobalt nitrate, when aluminium oxide or other heavy metallic oxides are absent.[13] When a mixture of neutral cobalt chloride and magnesium chloride is treated with ammonia a green precipitate forms, which contains nearly 10 per cent of magnesium oxide, remains green upon washing, is insoluble in ammonia and ammonium carbonate, but slightly soluble in ammonium chloride imparting a dirty yellow color, and can be reprecipitated by potassium hydroxide.[13]

$(Mg.Co)O.Al_2O_3$—On fusing 5 parts of Al_2O_3, 2.4 parts MgO, 20 parts CoO and 4.7 parts fused B_2O_3 in a platinum dish and dissolving the flux in hydrochloric acid, regular octohedra remain which will scratch glass. When less cobalt is used blue spinels form.[14,15]

$2MgO.CoO.B_2O_3$—Made by Ebelmen[16] according to Mallard's[17] method. The product is composed of an isomorphous mixture of $3(MgO.CoO)2B_2O_2$, which according to Guertler[18] possesses the formula $2(MgO.CoO)2B_2O_3$, since the formula of the compound $3MgO.2B_2O_3$ in reality is $2MgO.B_2O_3$.

$3CoO.2B_2O_3.4H_2O$—Formed by precipitating cobalt sulfate with borax. Color, reddish white.[19]

$3CoO.B_2O_3$—Made by fusing cobaltous oxide with B_2O_3. Rose-red rhombic crystals form.[16] Formula corrected by Guertler to $2CoO.B_2O_3$.[18]

$CoO.Al_2O_3$—COBALTOALUMINATE—When aluminium oxide is heated with cobalt nitrate or when a mixture of iron-free alum and a cobalt salt is precipitated with an alkali, a bright blue precipitate forms.[20]

THENARD'S BLUE—The composition varies, depending on the method of manufacture. Sometimes it is cobaltous oxide and aluminium oxide; other times it is phosphate or arsenate of cobalt. It is best prepared by first precipitating a solution of a cobalt salt, usually the iron- and nickel-free nitrate, with potassium or sodium phosphate or with sodium arsenate. The gelatinous, violet precipitate is thoroughly washed and well mixed with 3 to 5 volumes of freshly precipitated, well-washed alumina (when cobalt arsenate is used a larger proportion of alumina may be added), precipitated from a solution of iron-free alum by the addition of sodium carbonate. The mixture is dried until it becomes brittle, and heated at a cherry-red heat for 30 min. in a covered clay crucible. When the desired blue color has been developed, the mass is ground with water and dried. In order to prevent the possibility of entrance of reducing gases, which would injure the value of the product Regnault[21] recommended the addition of a little mercuric oxide before the ignition. This decomposes and evolves oxygen, which prevents reduction. The mercury escapes in the form of vapor.

A similar but less fine product is produced by the simultaneous precipitation of the oxide of cobalt and aluminium by the addition of sodium carbonate to a mixture of cobalt nitrate and alum. The mixed precipitate is washed and treated as above.

According to the process recommended by Binder,[22] the oxide of cobalt is precipitated by the addition of the requisite quantity of ammonia to a solution of pure cobalt chloride. The washed precipitate is mixed with alumina as before, dried, and heated at red heat in a clay crucible for 2 hrs.

Thenard's blue is of a fine ultramarine color. The presence of an excess of cobalt imparts a somewhat greenish tinge. It is one of the most permanent blue pigments, being unaltered by acids and alkalies, and is largely used as an oil and water color, though it works better in water alone. It is nonpoisonous, and has the advantage of miscibility with other pigments without alteration.

RINMANN'S GREEN—The first contributions concerning Rinmann's green were made in the year 1780, when S. Rinmann described one of his newly discovered green pigments, which he recommended as a paint color because of its resistance to atmospheric conditions. It appeared that Rinmann was searching for this green pigment, for in one place he writes that he considered it possible to fix the greenish blue color of certain cobalt solutions. He had in this connection tried zinc oxide as a fixing agent, for he precipitated a cobalt and zinc solution with

---

[1] Received April 4, 1921.

[2] This paper represents work done at New York University and the University of Cincinnati in partial fulfilment of the requirements for the degree of Master of Science at New York University.

[*] Numbers in text refer to Bibliography.

calcium carbonate, dried the precipitate and ignited it, and found that the green color obtained corresponded in minutest detail to the color of the above-mentioned cobalt solution. He observed that the mass became green at low red heat, but upon being more strongly ignited and subsequently cooled it again turned gray and finally black.

As a possible explanation of the blue-green color, Rinmann assumed the existence of a colored modification of cobalt oxide, the green substance being an additive compound of this blue compound with a yellow metallic oxide. However this explanation did not hold when other oxides were examined. It is, however, of interest to note in connection with the explanation which is to follow, that Rinmann had suspected this substance to be of a mixed color.

From the end of the eighteenth century to the middle of the nineteenth, however, one searches in vain for information concerning Rinmann's green. The industrial investigations concerning this substance have been carried out technically rather than chemically. At best, one finds only very indefinite suppositions concerning the reactions involved.

Researches by Hedvall[23] with a view to preparing Rinmann's green in crystalline form, resulted in the formation of cobaltous oxide crystals in octahedral and prismatic form, similar to those obtained by Lachaud and Lepierre. Hedvall found that he could obtain well-defined cobaltous oxide crystals by heating ordinary cobaltous oxide or cobaltous carbonate several times to 1000° or higher, with, say, four times its weight of potassium chloride. By this method, there are obtained exceedingly beautiful crystals of cobaltous oxide enclosed in the Rinmann's green. They have a dark red color, and the majority of them seem to be octahedra, tetradehra, and a combination of positive and negative tetrahedra. Very often the cobaltous oxide crystals enclosed in the crystals of Rinmann's green are surrounded by a brighter green region than Rinmann's green. Often they are embedded in the cobaltous oxide.

Hedvall has accepted an hypothesis of L. Storch[24] to explain the color of Rinmann's green. According to Storch, there exists a blue modification of the lower oxide of cobalt which gives a green color with the yellow zinc oxide. This blue modification is not stable unless zinc oxide is present. It is thought that Rinmann conceived of it as early as 1780. One meets it again in the work of J. Bersch. Doubtless the opinion is a relic of the time when chemists established the properties of the metallic oxides from those of the salt. In any event, it is not very probable because: (1) This blue modification has never been prepared; (2) zinc oxide is yellow when hot; crystalline zinc oxide is exceedingly pale yellow with a tinge of green. This color change rests upon the fact that the absorption spectrum of the zinc oxide moves with the rise of temperature from the ultraviolet to the visible part of the spectrum and not upon the formation of a new modification. Such shifting of the absorption spectrum with the temperature is quite general.

In nature, crystalline zinc oxide occurs as the rare mineral zincite, which crystallizes in hexagonal semimorphous prisms and pyramids. Gorgeu[25] states that by heating zinc sulfate with an alkali sulfate there are formed greenish yellow, hexagonal prisms and tablets with high refractive index.

The question which deserves consideration is: Is Rinmann's green a compound, and in what way is one to conceive of its structure? The substance was made by Hedvall from a mixture of zinc and cobalt carbonate or oxalate, or the oxide mixture which results from the heating of the salts. This mass was again heated with or without a flux of potassium chloride to 1100° and 1300° to 1400°. A platinum crucible was used in every case since it was shown that the cobaltous oxide united with the silicate glaze of porcelain crucibles.

When Rinmann's green is prepared according to this method the contents of the crucible become greenish yellow even at red heat. The mass is not molten and does not appear homogeneous. Upon cooling, the surface becomes grayish black, the inner part retaining its yellowish green color. At white heat, the color becomes almost green when proper proportions of the oxide have been used, and the color is not changed when cooled in an atmosphere of carbon dioxide; when cooled in air, however, the surface becomes black, as a result of the formation of Co_3O_4.

In all these experiments Hedvall found that in a blast furnace at 1100° or in a porcelain furnace from 1300° to 1400° Rinmann's green and its two components, cobaltous oxide and zinc oxide, were always obtained in crystalline form. When no fusion mixture was used, large crystals or a homogeneous mass did not result. The product was composed of exceedingly small crystals of Rinmann's green and one or both of the components. That they were crystalline could be observed when magnified in polarized light. From this experiment, it was thus possible to prepare Rinmann's green in crystalline form.

An attempt was made to separate the components of the melt, namely, cobaltous oxide and Rinmann's green. This was not possible with chemical reagents, as all the solvents tried, such as hydrochloric, sulfuric, nitric, and acetic acids, potassium hydroxide, ammonium hydroxide, ammonium carbonate, and potassium cyanide, reacted upon the cobaltous oxide as well as upon the Rinmann's green. A preliminary determination showed that the specific gravities of these two substances are too high and too near each other to accomplish a separation in this way. To get larger crystals of Rinmann's green, the usual methods were pursued, *i. e.*, the addition of a fusion mixture and slow cooling.

In this connection many substances were examined. With calcium chloride and B_2O_3 it has been proved that a cobalt borate is formed, and upon boiling the flux with potassium carbonate a characteristic green solution is formed, probably of the same kind as that obtained by the decomposition of cobaltous hydroxide. The percentage figures of flux are so computed that the original mixture of zinc oxide and $CoC_2O_4.2H_2O$ corresponds to 100 per cent. When a mass is quoted as being CoO-0.3, ZnO, 100 per cent ICl, it denotes the presence of one molecule of CoO to three molecules of ZnO; for example, 1 g. CoO (1/75 mole = 2.49 g. oxalate or 1.55 g. carbonate) corresponds to 3.25 g. ZnO (3/75 moles) and 5.7 g. KCl. In order to investigate under what conditions the largest and best shaped crystals are formed a series of experiments were carried out, partly with different mixtures of flux and partly with varying amounts of the two oxides. Hedvall found that a mass of the composition 1 CoO.1 ZnO with 60 to 70 per cent KCl was not yet molten at 1100° C., and only a few crystals of Rinmann's green and cobaltous oxide had formed. Often these fused together, and well-defined crystals formed from the inside of the crucible in a remarkable fashion, from 0.5 to 1 cm. large. They collapsed, however, as soon as they were boiled with water. This same mass was then heated at the same temperature with 100 per cent potassium chloride for 3.5 hrs. and cooled in carbon dioxide. After removing the flux a dark green substance remained, composed of red and green crystals. Some of the green crystals were large and well defined and made up of hexagonal plates or pyramids of a beautiful green color. Frequently a zone structure could be observed. The red crystals often appeared enclosed in the green and were well-formed octahedra or tetrahedra. With this last proportion of flux and oxides and at this temperature, therefore, a well-crystallized Rinmann's green can be formed.

Since the yield of large crystals was very small with only one ignition, the operation was repeated several times. Each time new mixtures of flux were added during ignition, and between each heating the mass was boiled out in order to accomplish thorough mixing, without crushing the larger crystals already formed. Each ignition lasted from 1 to 2 hrs., and after repeated ignitions the yield was increased, as well as the formation and size of the green crystals.

The little red crystals were washed but little at first. The different size of the green and red crystals made it seem possible to separate them with a sieve whose mesh was large enough to let the small crystals through and to retain the large ones. A completely homogeneous Rinmann's green could not be obtained in this way, however, for many of the red crystals are enclosed, as mentioned before, and these, of course, could not be removed. A uniform red substance was naturally impossible to get in this case. However it was possible to make a few tests.

The green crystals were washed in the usual manner preparatory to the analysis. A weighed amount of substance was dissolved in hydrochloric acid, the solution heated, and the escaping gases were dissolved in potassium iodide solution. By this treatment no iodine came off; therefore no peroxide could be present. Rinmann's green, therefore, contained only divalent cobalt.

Analysis of Red Crystals—It is natural to suspect that the red crystals are composed of cobaltous oxide. The strongly heated cobaltous oxide, as mentioned before, is very insoluble in acids. The crystals of Rinmann's green are easily soluble even in weak acids. A small amount of the above-mentioned mixture, after passing through the sieve, was treated for 12 hrs. with acetic acid and filtered from insoluble substance. The insoluble substance appeared entirely homogeneous under the microscope and consisted of crystals which looked like cobaltous oxide crystals. This substance was not completely soluble in concentrated hydrochloric acid. Only upon treatment with concentrated sulfuric acid did it go entirely into solution.

Even upon treating the residue with acetic acid, no zinc could be detected. An analysis was carried out on a weighed amount of this residue, 0.1631 g. (insoluble in acetic acid) gave 0.1272 g. of Co = 78.47 per cent cobalt, computed as CoO = 78.67 per cent. Cobalt as a metal was identified after reduction in a stream of hydrogen.

In order to ascertain where the boundary lay for complete reaction between the zinc oxide and the cobaltous oxide a series of masses (1.7 moles ZnO to 1 mole CoO with 100 per cent potassium chloride) were heated in a porcelain furnace in sealed tubes.

Von Delasse has given a method for determining the percentage composition of stone containing more than one mineral. Later his method was simplified by A. Rosival. The number of scale parts was calculated which was due to each constituent in a preparation. This number (a uniform division of the constituents was assumed) was set in proportion to the volume of substance concerned. When the specific gravity of the total material and of each constituent was known, it was easy to go from the per cent volume to the per cent weight. Thus a large number of scale divisions were calculated. Taking the Constituents A and B, for example, and considering each scale division as a and b:

$$\text{Per cent volume A} = \frac{100a}{a+b}$$

$$\text{Per cent volume B} = \frac{100b}{a+b}$$

If now the specific gravity of the total substance (A + B) = S, from which A = S_A and B = S_B we have:

$$\text{Per cent weight A} = \frac{100a.S_A}{(a+b)S}$$

$$\text{Per cent weight B} = \frac{100b.S_B}{(a+b)S}$$

If $(a + b)$ is a larger number and the preparation is as homogeneous as possible, the accuracy of this method is then sufficient to warrant combining the results of this calculation with those of chemical analysis.

To carry out this impurity calculation, microscopic preparations were made, two for each fusion. These were so prepared that the melt could be ground or the purified mass of flux be divided on the object glass, in powdered form. When the cover glass was put on the object glass, part of the preparation spurted off toward the edge. This portion was gathered and put on a second slide so that the calculations gave the same proportions as in the preparation at hand. Much effort was required to get a uniform diversion, and the mixture index was very great in each case (4–10,000 scale divisions). The fusion was always removed from the slides which were prepared for an analysis. All the calculations were carried out with a Zeiss microscope with a 760 enlargement.

From several of these determinations Hedvall concluded that Rinmann's green had no definite composition. If, then, Rinmann's green is not a chemical compound, it may be a case of solid solution. If one accepts zinc oxide as a solvent, it then follows that we are dealing with a dilute solution.

Action of Flux—From what has preceded it is clear that the fusion mixture is of the greatest importance to the growth and formation of the crystals. In some of the fusions, the fusion mixture was increased 100 per cent. The same proportions of zinc oxide and cobaltous oxide were used as in the former cases. From a mass of 0.1 CoO, 0.1 ZnO with 100 per cent potassium chloride, only small, poorly shaped crystals were obtained. With 100 to 200 per cent potassium chloride, large hexagonal prisms and tablets were formed. This relation held only for the above-mentioned fusions. With increasing amounts of zinc oxide the formation of needle-shaped crystals became proportionately difficult. Often the crystals separated from the melt as skeletons. It is evident that these different crystalline forms are dependent on the different viscosities of the fusion mixture. It is also evident that the reaction between the two components, cobaltous oxide and zinc oxide, is entirely or nearly complete, in the presence of fusion mixtures so that only one compound occurs with the Rinmann's green, while in the mass without fusion mixture Rinmann's green and both components are present.

To prove this, Hedvall divided a mixture of 1 CoO : 3 ZnO into two equal parts. To Sample 1, 100 per cent potassium chloride was added; to Sample 2, no flux was added. Both were heated three times at 1100° under the same conditions. Between each ignition the substances were well mixed and a new portion of potassium chloride was added to Sample 1 to replace that which had volatilized. After Sample 1 was freed from flux slides were made of each. Calculations were made in the usual way.

Two methods were used to obtain analyzable material. One was based on the fact that Rinmann's green crystals grow on successive heatings, while cobaltous oxide crystals do not. To get a product as pure as possible by this method, a mass was used which would contain cobaltous oxide in excess inasmuch as zinc oxide would be much more difficult to separate. In this way, the yield became very small. After some fifteen or twenty heatings, about 3 per cent of the calculated mixture was retained and this process took about a week. The crystals were prepared for analysis, while the flux was being removed with water. The crystals were then washed on the sieve with anhydrous benzene in order to remove the cobaltous oxide crystals as much as possible. The substance was then pulverized, thoroughly mixed in an agate mortar, and analyzed. At the same time an impurity calculation of the substance analyzed was carried out on a microscope slide.

The other method corresponded with the one of heating in a porcelain furnace. Most of the fusions which were made resulted in products which were of such a high degree of purity as to warrant analysis by the microscopic method. The slides were prepared from the mass used for analysis. The values obtained were not the same as those which were prepared from the fusion. It is reasonable of course to expect that the substance after much washing did not have the same composition as it had before.

Determination of Specific Gravities—As was previously stated it was necessary to know the specific gravity of these different substances in order to be able to calculate the amount of impurity. These determinations were carried out in benzene (sp. gr. 1.8847 at 17.5° C.). Determinations were made with crystals of cobaltous oxide and zinc oxide formed at 1100° and 1300° to 1400°, respectively.

In some cases the specific gravity of Rinmann's green was between those of the constituents. In other cases it was lower than that of the constituents. The deviation, however, was small. Aside from these, differences between the specific gravity of the flux and that of the components below it were so small that the calculated impurity could be used with safety. In most fusions the impurity was so small that it was negligible in the analysis error. Summarizing these facts, Hedvall concluded that the different fusions gave Rinmann's green of varying composition. From this it is clear that these substances can be no chemical compounds but rather a solid solution between the two components, cobaltous oxide and zinc oxide. These two substances form with each other a series of mixed di-isomorphous crystals; while zinc oxide crystallizes hexagonally, cobaltous oxide in general, at least, crystallizes regularly. Only in a few cases where the larger crystals of Rinmann's green were obtained was it possible to determine crystal structure and in those cases it was hexagonal. Whether or not it gave a regular form (with large mixtures of cobaltous oxide) was not proved; at least, not in the fusion of 1 CoO and 1 ZnO. At any rate, according to Weber, a regular crystalline form of zinc oxide is known.

It can be concluded from the investigation that the formation of Rinmann's green takes place at red heat, but much more quickly at higher temperatures. It is not necessary, however, that the mass liquefy, for the masses which do not contain flux give a Rinmann's green of the same appearance; but in this case the conversion between the cobaltous oxide and the zinc oxide is not complete. We have here, then, in all probability an example of diffusion in solid substances.

$CoO.V_2O_5$—COBALTOVANADATE—Normal vanadate yields a reddish yellow precipitate with cobalt salts. Acid cobalt vanadate is water-soluble and when treated with acid in aqueous solution a reddish yellow precipitate forms. (Berzelius.[13])

When cobalt nitrate is treated with ammonium metavanadate in a completely neutral solution it yields an orange-yellow precipitate. When heated it has the composition $CoO.V_2O_5$. Cobaltovanadate can also be formed by the conversion of potassium vanadate with cobalt salts.

$CoO.V_2O_5.H_2O$[26,27]—This substance may be prepared by displacing ammonium vanadate with an excess of cobalt nitrate in acid solution with nitric acid, and warming. Garnet-red, rhombic prisms form which are soluble in water.[28] When heated, the color becomes darker with loss of water. According to Radau[27] it is not probable that normal vanadate forms under the conditions just mentioned.

$CoO.2V_2O_5$—An ammoniacal solution of cobalt salt gives with NH_4VO_3 a greenish precipitate, which on exposure to air takes up oxygen. At 100° it becomes reddish brown and upon heating a black product is formed of the above composition(?).[26]

$K_2O.2CoO.5V_2O_5$ (16 OR 16.5 H_2O), POTASSIUM COBALTOVANADATE—This substance forms when a 20 per cent solution of KVO_3 is mixed at room temperature with 100 cc. of cobalt sulfate solution containing 18 g. of the salt. A reddish yellow crystalline precipitate forms which is slightly soluble in water and completely soluble in acids. It can also be prepared by mixing a solution of 20 g. KVO_3 in 200 cc. water with a solution of 20 g. cobalt sulfate in 200 cc. water; after warming on the water bath, 70 cc. of 25 per cent acetic acid are added, whereby the yellowish red precipitate which first forms redissolves. The dark red solution yields glistening, brownish red crystals.

Another method of preparation consists of mixing a solution of 16 g. of $3K_2O.V_2O_5.10H_2O$ in 400 cc. water with a solution of 11 g. of cobalt sulfate in 150 cc. boiling water, stirring and digesting for some time. The dark red solution yields garnet-red crystals, which lose one-fourth of their water at 120° and the remainder at 220°. This product is also formed when 12 g. of potassium divanadate are dissolved in 250 cc. boiling water and mixed with 8.5 g. cobalt sulfate in 100 cc. of water. Dark red crystals, having properties similar to those just mentioned, form. 4.8 parts of the substance dissolve in 100 parts of water at 17.5°.[29,27]

$K_2O.3CoO.7V_2O_5.21H_2O$—Prepared by mixing a solution of 20 g. of KVO_3 in 400 cc. of water with 18 g. of cobalt sulfate in 250 cc. of water. At first no precipitate forms, but the solution becomes turbid on standing. Upon evaporation, brown crystalline crusts form, along with little yellowish brown crystalline needles which can be separated from each other mechanically. The latter crystals are the ones sought for.[27]

$6CoO.P_2O_5$—Prepared by heating Braun's so-called luteocobalti metaphosphate, which becomes rose-red upon the addition of concentrated sulfuric acid and red when treated with sodium hydroxide; after removing the sodium hydroxide, the residue for the most part soluble in hydrochloric acid. The undissolved part is a beautiful red and is the product sought for.[30]

$3CoO.2P_2O_5$—COBALTOPYROMETAPHOSPHATE—Remains as a violet powder when $[Co(NH_3)_5].(PO_4H)_3.4H_2O$ is heated. Contains 43.58 per cent CoO.[30]

$7CoO.As_2O_3$—COBALTOARSENITE—When $Na_2O.As_2O_3$ is treated with an excess of cobalt nitrate the following reaction takes place: $7Co(NO_3)_2 + 2(Na_2O.As_2O_3) + H_2O = Co_7As_2O_{10} + 12NaNO_3 + 2HNO_3 + As_2O_3$.

When freshly precipitated, a slimy, very voluminous amethyst-colored mass forms, which upon drying in the air contains 20 per cent of water, losing it at 150°. It is soluble in sodium hydroxide and ammonia, and very soluble in dilute, and sparingly soluble in concentrated, sulfuric acid. When suspended in water and shaken, or better, warmed with barium peroxide it becomes leather-yellow, then brown, and finally black (formation of Co_2O_3). This substance is also very soluble in potassium cyanide, from which it can again be precipitated by acids; barium peroxide does not decompose it in the presence of potassium cyanide.[31,32]

$3CoO.As_2O_3.4H_2O$; OR $Co_3(AsO_3)_2.4H_2O$—COBALTORTHOARSENITE—This substance forms when a 50 per cent alcoholic solution of cobalt chloride is treated with a solution of potassium arsenite made neutral with acetic acid. A bright red precipitate forms which is sparingly soluble in water, but readily soluble in acids. It turns black upon heating.[33]

$2CoO.As_2O_3$ OR $Co_2As_2O_5$—COBALTOPYROARSENITE—According to Proust,[7] this substance seldom forms in the interior of erythrite. It is prepared by mixing dissolved cobalt salt with potassium arsenite containing cobalt arsenite. A rose-red precipitate forms which becomes dark and horny on drying. That which is precipitated by $2K_2O.As_2O_3$ is also $2CoO.As_2O_3$.[34]

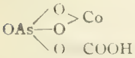
From cobalt nitrate and $Na_2As_2O_4$ a violet-blue precipitate forms, which loses arsenious oxide upon heating and leaves a dark blue residue.[35] It forms when cobalt chloride solution is treated with potassium pyroarsenite, $K_4As_2O_5.6H_2O$, as described by Girard.[34,33] If heated in glass vessels arsenious oxide is evolved and colors the glass blue; when treated with a hot solution of potassium hydroxide, it decomposes into cobaltous hydroxide and a blue solution, from which water precipitates the cobaltous hydroxide. It is soluble in nitric acid with evolution of nitrosylsulfuric acid, soluble in hydrochloric acid, and in ammonia, with a dark red color. It is soluble in potassium hydroxide and sodium hydroxide, only when in the nascent state.

It can also be prepared by adding potassium stannite with large excess of potassium hydroxide to a cobalt solution.[36,37]

$3CoO.2As_2O_3.4H_2O$—This substance forms with evolution of much ammonia when potassium arsenite is rapidly added to a solution of cobalt chloride which has been mixed with an excess of ammonium chloride.[34] It can also be prepared by treating a cobalt salt solution with $K_2O.2As_2O_3$.[35] The fresh precipitate, pale rose-red, gradually becomes heavier and darker, first loses water upon heating with darkening of color, and then arsenious oxide, leaving a beautiful blue flux; upon cooling a solid crystalline residue remains. Potassium hydroxide decomposes the precipitate when heated, with separation of blue cobaltous hydroxide; hydrochloric acid decomposes it and converts it into an arsenate. At 100° it loses 10.3 per cent H_2O ($4H_2O$ = 10.39 per cent).[34] When treated with ammonia a brownish red solution results, and when treated with potassium cyanide a yellowish red solution is produced.[35] Stavenhagen[33] could not obtain $Co_3As_4O_9.4H_2O$ by rapid addition of $K_4As_2O_7.2H_2O$ to a solution of cobalt chloride.

BASIC $4CoO.As_2O_5$ (WATER-FREE) COBALTOARSENATE—Forms when a solution of cobaltoarsenate, acid with nitric acid, is treated with sodium carbonate. When fused in a porcelain oven cobaltoarsenate crystallizes completely into beautiful prisms. They are deep dark blue; rose-red when powdered, and readily soluble in acids.[38]

The commercial cobaltoarsenate is formed as *chaux metallique* by precipitation of a solution of cobalt nitrate with potassium carbonate, from which $FeAsO_4$ has previously been removed by precipitation. It can also be prepared by the repeated fusion of glossy cobalt with iron-free potassium arsenocobalt, which is then roasted until it is all changed into a red powder.



(With 1 mole H_2O)—Prepared by heating an excess of cobalt nitrate solution with sodium arsenate in a sealed tube at 180°. Orthorhombic, blue and reddish violet crystals form.[39,40]

$Co_3(AsO_4)_2.8H_2O$, NORMAL—Occurs in native state as erythrite. The erythrite forms small tuft-like groups of long monoclinic needles, semitransparent, crimson or peach blood-red, and very uniform. Upon drying it is a deep lavendar-blue in color.[41]

It forms as a peach blood-red substance which dries to a dark horny mass when a cobalt salt is precipitated with sodium arsenate.[42]

$Co_3(AsO_4)_2.8H_2O$, ACID—When evaporated in vacuum over sulfuric acid, solutions of cobaltous hydroxide or the normal cobaltoarsenate in excess arsenic acid yield peach blood-red, star-shaped needles, uniting in clusters similar to erythrite, but soluble in water.[43]

$5CoO.2As_2O_5.3H_2O$—When cobaltous carbonate is digested with an excess of arsenic acid solution and the liquid heated in a sealed tube at 235°, pale rose needles form, insoluble in water, and losing their water at high temperatures.[39]

$2CoO.As_2O_5$, WATER-FREE—Prepared from potassium metarsenate and a little cobaltous oxide from which violet knobbed crystals form.[44] When more cobaltous oxide is used, potassium cobaltorthoarsenate yields $2CoO.K_2O.As_2O_5$; upon the addition of cobalt chloride, somewhat opaque, blue crystals form. With sodium instead of potassium, violet, leaf-shaped crystals of $4CoO.2Na_2O.3As_2O_5$ form. Upon the addition of sodium chloride to the orthoarsenate, $CoO.2Na_2O.As_2O_5$, blue transparent prisms form, isomorphous with the manganese and cadmium salts.

COBALT ANTIMONITE—A pale violet, noncrystalline powder is obtained which turns dark green on heating, with loss of water; on strong heating it glistens and possesses a white color and is sparingly soluble in water.[13]

$CoO.Cr_2O_3$—COBALTOCHROMITE—This substance is prepared from a hot solution of cobalt chloride and chrome alum (equivalent quantities) with sodium carbonate, and the bluish gray precipitate is heated. Beautiful dark green crystals form which lack metallic luster and magnetism.[20]

$CoO.2MoO_3.2H_2O$—ACID COBALTOMOLYBDATE—Forms at 100° from $2CoO.4MoO_3$. When heated with a blast lamp it loses water and MoO_3 and changes to the normal violet salt.[45]

$2CoO.4MoO_3.13H_2O$—Forms in considerable quantities as microscopic brown needles, very sparingly soluble in water, after separation of $CoMo_4.H_2O$ from equivalent solutions of $Na_2O.2MoO_3$ and $CoCl_2.6H_2O$.[45]

$CoO.3MoO_3.10H_2O$—Forms when cobaltous carbonate is boiled with an excess of MoO_3 and the solution allowed to evaporate spontaneously. Cauliflower-like knobs of a rose-red color form, sparingly soluble in cold, very soluble in hot water.[46]

$3CoO.7WO_3.25H_2O$—SO-CALLED PARATUNGSTATE—Formed by the addition of boiling sodium paratungstate solution to a cobalt sulfate solution (not the reverse, which results in the formation of double salts). From a fine-grained precipitate it changes to an oily viscous dough-like, rose-red mass of silky luster. The latter solidifies on cooling to a firm powdery mass of the same composition as the fine-grained product, and is bright rose in color, microcrystalline, infusible at red heat, and takes on a bluish color on cooling.[47]

CONCLUSION

On examination of the descriptions of the compounds of cobalt, it is at once obvious that for the most part, they fall into two classes with respect to color: red and blue. The red salts are generally hydrated, and the red hydroxide is the one stable in presence of alkali. The blue salts are generally anhydrous, and the blue hydroxide is stable in the absence of alkali, or in the presence of cobalt salt or cobalt ion.

The writer is doubtful of the correctness of designating many of the combinations as "compounds." In many cases, where these are amorphous they are probably adsorption coagula, and where they are crystalline they are probably mixed crystals whose composition is simple, fortuitously, or because equivalent ratios of constituents were used in their preparation. The very complete research on Rinmann's green illustrates the case of mixed crystals.

Without any intention of exaggerating the analogy, a certain similarity may be noted between tautomeric forms of organic indicators and the two forms of cobalt hydroxide. For example, there is the colorless phenolphthalein, its colorless esters and polysodium salts, and the colored phenolphthalein esters, monosodium salt, and insoluble silver salt. This indicates the inadequacy of any assumptions as to ionization or hydration as an explanation of the color or lack of color of these compounds, and throws the explanation back to the structure theory. Since all phenolphthalein compounds are colorless or red in the absence of other chromophores, so all cobalt oxide compounds, solid solutions, or mere agglomerates are either blue or red, provided no other chromophores are present.

Application of the methods of the recent work done on X-rays and crystal structure will furnish conclusive evidence as to the correctness of this theory. Until such data are available the classification just given must suffice.

BIBLIOGRAPHY

1—Zimmermann, *Ann.*, **232** (1886), 339.
2—Russell, *Chem. News*, **7** (1863), 43.
3—Moissan, *Ann. chim. phys.*, [5] **21** (1880), 243.
4—Playfair and Joule, *Mem. Proc. Chem. Soc. London*, **2** (1845), 401, **3** (1848), 57.
5—Lachaud and Lepierre, *Compt. rend.*, **115** (1892), 115; *Bull. soc. chim.*, [3] **7** (1892), 600.
6—Beetz, *Pogg.*, **61** (1844), 472.
7—Proust, *J. phys.*, **63** (1806), 421.
8—Fremy, *J. Pharm.*, **19** (1851), 404.
9—Fremy, *Jahresber.*, **19** (1851), 637.
10—De Schulten, *Compt. rend.*, **109** (1889), 266.
11—Tubandt, *Z. anorg. Chem.*, **46** (1905), 37.
12—Hantzsch, *Z. anorg. Chem.*, **73** (1912), 304.
13—Berzelius, *Pogg.*, **33** (1834), 126.
14—Ebelmen, *Mem. presentes divers Savants, Acad. roy. sci.*, **13** (1852), 561.

15—Ebelmen, *Ann. chim. phys.*, [3] **33** (1851), 67.
16—Ebelmen, *Ann. chim. phys.*, [3] **33** (1851), 34.
17—Mallard, *Ann. mines*, **171**, [8] **12** (1887), 457.
18—Guertler, *Z. anorg. Chem.*, **40** (1904), 240.
19—Rose, *Pogg.*, **88** (1853), 299.
20—Elliott, "On the Magnetic Combinations," Göttingen, **1862**, 33.
21—Regnault, "Cours Elementaire de Chimie," **3**, 150.
22—Binder, "Technologiste," **5**, 55.
23—Hedvall, *Z. anorg. Chem.*, **86** (1914), 201.
24—Storch, *Deutsch. naturw. med. Ver., Prag.*, **8** (1912), 57; *Chem. Zentr.*, **83** (1912), 1523.
25—Gorgeu, *Jahresber.*, **1858**, 182.
26—Carnot, *Compt. rend.*, **109** (1889), 148; *Ber*, **22** (1889), 652.
27—Radau, *Ann.*, **251** (1889), 114.
28—A. Ditte, *Compt. rend.*, **104** (1887), 1705.
29—Fock, *Z. Kryst. Mineralog.*, **17** (1890), 11.
30—Braun, "Ammoniak-Kobaltverbindungen," Göttingen, **1862**, 39.
31—Reichard, *Z. anal. Chem.*, **42** (1902), 10.
32—Reichard, *Chem-Ztg.*, **26** (1903), 1145.
33—Stavenhagen, *J. prakt. Chem.*, [2] **55** (1895), 39.
34—Girard, *Compt. rend.*, **34** (1852), 918.
35—Reichard, *Ber.*, **31** (1898), 2163.
36—Reynoso, *Compt. rend.*, **31** (1850), 68.
37—Reynoso, *Jahresber.*, **3** (1850), 316.
38—Gentele, *Oëfvers. Kgl. Vet. Acad. Forhandl.*, **8** (1851), 123; *Jahresber.*, **1851**, 159.
39—Coloriano, *Compt. rend.*, **103** (1886), 274; *Jahresber.*, **1886**, 365.
40—Buchrucker, *Z. Kryst. Mineralog.*, **19** (1891), 113.
41—LaValle, *Atti acad. Lincei*, [5] **7** (1898), II, 68; abstr. *Chem. Zentr.*, **69** (1898), II, 790.
42—Gmelin-Kraut, Freidheim, V, Part 1, 7th edition.
43—Kersten, *Pogg.*, **60** (1843), 266.
44—LeFevre, *Compt. rend.*, **110** (1890), 407; *Jahresber.*, **1890**, 501.
45—Marckwald, Dissertation, Basel-Berlin, **1895**, 15.
46—Ullik, *Ber. Wien. akad.*, **55**, 2, 767; *Jahresber.*, **1867**, 259.
47—Gonzolez, *J. prakt. Chem.*, [2] **36** (1887), 49.

SOCIAL INDUSTRIAL RELATIONS

A Method for Social Research

By **H. W. Jordan**

SYRACUSE, N. Y.

In ancient days thunder and lightning were believed to be the work of Jove or Thor. Plagues were thought to be the hand of God laid upon mankind in punishment. Bountiful crops or famine years were similarly regarded as expressions of Divine good will or wrath. Whatever was not understood was believed to be superhuman and impossible of control by man. Individuals and nations submitted to these manifestations of natural force, without question, until men of theoretical science disclosed the laws of electricity, contagious disease, and plant growth; and chemists or engineers followed who applied the theoretical science to the day's work.

The result, nearly all attained within the past fifty years, was evolution of the huge engineering industries which to-day are so commonplace that even the two seemingly superhuman ones, wireless telegraphy and aviation, are in daily commercial use. Each has been reduced to an exact science, which varies in its results only as man is unable to hold the helm true to an unswerving course in an open sea.

THUS THE PHYSICAL FORCES THAT USED TO TERRIFY AND DESTROY have been transformed into power that drives the world's industry.

During this half century of tremendous material transformation, by science applied through research, the forces that direct government, banking, commerce, secondary education and most other mental or spiritual activities, outside applied science, continued to guide these functions in accordance with the ancient belief that individual or national action is subject to few, if any, fixed laws discoverable by man. The leaders of government and commerce saw no analogy between the modern industrial world and the perfect social organizations of the ants or the bees, in which complete specialization of the individual is made completely effective by coöperation. They failed to discern that the new, intricate problems of human relations that arise from complex, industrial, city life can also be solved by science and research as chemical problems are. As they did not grasp this fact, these leaders continued to apply, with few changes, the methods of government and social control that had prevailed since the days of Rome and of England before Watt and Arkwright.

They regarded government, commerce, and social industrial relations as things outside the scope of improvement by experiment and scientific research. They believed each human mind to be a free and independent unit, subject to no general or mass mind law.

WITHIN THE LAST TWO DECADES scientists have appeared who have proved the close similarity of material and mental forces. They have shown that one primary mechanical law and several laws of biology govern the action of the entire modern industrial world. One of these practical scientists, Roger W. Babson, a Massachusetts Institute of Technology engineer, has applied the mechanical law of equal action and reaction so successfully as a guide in commerce and industry that more than fifteen thousand individuals, banks and business organizations pay total fees approaching two million dollars annually for Mr. Babson's mathematical interpretation of equal action and reaction applied to the ebb and flow of the world's industry and trade.

The Babson Statistical Organization has become one of the greatest international forces for attainment of peaceful, scientific commerce, of practical secondary education and of world realization of the Golden Rule—which is the law of equal action in human relations.

How has Mr. Babson accomplished this? Simply by sticking to the supreme conviction that the law of equal action applies as completely to all human action as it does to the steam engine or dynamo. And by putting this conviction to the scientific research test of trying it upon a score of people, then upon a few hundred and now upon thousands, with the result that this law has become accepted by the hardest-boiled financiers and business executives, who pay liberally for this service of applied science and direct their mining, manufacturing, buying, and selling in accordance with the flow of the world's mental tide, accurately predicted and set down in Babson's nautical almanac of commerce.

FOUR OTHER LAWS THAT GOVERN HUMAN AFFAIRS have been brought to our attention, in addition to the law of equal action and reaction. We have often referred to them. They are of such extreme importance that we repeat them. They are:

1—That extreme specialization of the individual or nation (as in modern industry) which produce sincreased efficiency, leads to lack of adaptability; and that when specialization in any one direction goes so far as to unfit the organism for any condition of life except a single one, the chances of survival are greatly reduced and sooner or later the highly specialized organism becomes extinct or returns to a more generalized type.

2—That social or industrial specialization is destructive in accordance with this law of biology and evolution, unless, as in the social organization of the ants and bees, the specialization be correctly counterbalanced by complete social, industrial coöperation.

3—That when an extreme and sudden advance has been made in evolution, like the unprecedented development of engineering industry the past half century, its subsidence into the accepted daily order of living is followed by some other, resulting advance through evolution.

These laws are presented in detail by Edwin Grant Conklin in his invaluable book, "The Direction of Human Evolution."

4—Recently we have been given the law of human action by Korzybski, that man is a time binding creature, in contrast with the animals that are space binding, and vegetables that are material or element binding forms of life. And that social, governmental, and intellectual progress is dependent upon our observance of this time binding principle, in balance with the laws of equal action and of evolution above cited.

THESE LAWS PROVIDE A SOLID FOUNDATION FOR SOCIAL INDUSTRIAL RESEARCH. They are as fundamental to human progress as the laws of gravity, atomic weight, valence of the elements, and the benzene ring. How can we apply them?

Horace Greeley said, when resumption of specie payment occupied the front page after the Civil War, as disarmament does to-day, "The way to resume is to resume." The way to apply these laws is to apply them. Roger W. Babson has shown the way. He has organized a corps of people who study the whole subject of human industrial relations through statistics and translate the results of their research into language that every business executive understands—MONEY. By similar statistical analyses and by surveys, experimentation and science applied to human relations through research, we chemists and engineers can accomplish similar results throughout the entire social industrial field.

The Federated American Engineering Societies have located the road by their Research upon Elimination of Waste in Industry. The September issue of *Mechanical Engineering*, the journal of the American Society of Mechanical Engineers, in a summary of this work says, "The report discloses losses and waste due to the restraint and dissipation of the creative power of those who work in industry. It lays the foundation for knowledge of the destructive influences which have too much controlled the past. From this knowledge will grow the conviction that mental and moral forces must be added in a much larger degree to the physical resources now employed, if industry is to serve all who are dependent upon its continuous and effective operation."

This preliminary survey by the Engineers disclosed that, "Over 50 per cent of the responsibility of these wastes can be placed at the door of management and less than 25 per cent at the door of labor, while the amount chargeable to outside contacts is least of all."

IN OTHER WORDS, THE GREATEST PROBLEMS OF INDUSTRY TO-DAY ARE THOSE OF HUMAN RELATIONS.

Copies of the report can be obtained from The Federated Engineering Societies, 29 West 39th St., New York City. Every American chemist should study it.

The American Chemical Society, in coöperation with The Federated Engineers, should undertake systematic, persistent research in this field. Among subjects that require deep, serious study are, secondary education; production, distribution and manufacture of food and clothing; city housing; local city transportation; ownership, taxation and use of agricultural land in its relation to production of food and the raw materials of clothing and of housing; charity that coddles the effects, instead of eliminating the causes of subnormal humanity; and the influence of modern industry upon marriage and the vital and racial problems that arise from industrial city life.

CHIEFLY WE NEED TO MAKE DEEP RESEARCH TO EVOLVE A MODERN SYSTEM OF CITY, STATE, AND NATIONAL GOVERNMENT. "As things go now," says Alleyne Ireland in his book, "Democracy and the Human Equation," "we afford the peculiar spectacle of a people who apply twentieth century methods to twentieth century problems in engineering, chemistry, medicine, surgery and industry, and who in government approach the problems of the twentieth century with the theories and implements of the eighteenth century. What is now needed is that the special knowledge of the biologist, the psychologist, the sociologist and of the political scientist should be coördinated in an exhaustive inquiry into the form and function of government. The value of such an inquiry would be inestimable."

"Democracy and the Human Equation" is itself a study in government well worth careful reading. It should be studied in conjunction with Norman Angell's "The Fruits of Victory."

Such research constitutes the most vital part of the investigation upon Elimination of Waste in Industry.

Each of the subjects mentioned rides as a heavy load upon industry and is reflected in needless taxation, and in swiftly declining efficiency of the workers of all classes. To a large degree the conditions to be studied are avoidable causes of the social unrest that hampers industry. Collectively they steadily increase the cost of industrial production and reduce the mental and physical standards of living. That reduction reacts upon industry in restricted demand for superior goods, and in degenerated appreciation of art, literature, the drama, and all those higher objects of life that characterize advancing civilization and growing commerce. These high intellectual standards of life, placed within reach of the many, have made the United States the best market of the world.

THE MANAGEMENT OF INDUSTRY WILL COMMIT FINANCIAL SUICIDE IF IT IGNORES OR DESTROYS AMERICAN INTELLECTUAL STANDARDS.

As the chief purpose of Social Industrial Research is to ensure the continuance of profitable industry, its cost should be borne mainly by industry through voluntary contributions by contract in sufficient amount and for long enough time to assure conclusive results from the studies or experiments.

The research should be directed by the American societies of engineers and chemists. They, who are creators of modern industry, are best equipped to perform this lifesaving service.

The personnel for the detail of the study should be secured mainly from the greater universities and technical schools. The seniors and postgraduate students of the university departments of economics and social relations would be admirably suited for such social industrial research. The resulting coöperation of industry, engineers, and universities in these studies upon science applied to our greatest national social industrial problems would produce a new order of social education, as beneficial and creative as the order of technical education that has given us our entire staff of American chemists and engineers since 1870, who in turn gave us modern industry.

Ultimately and soon, various branches of Social Industrial Engineering would grow from this new applied science, and this century would be characterized by huge, splendid attainments in social, mental engineering, as the nineteenth century was by material engineering. Social Industrial Research, by coöperation of the engineering industries, the American chemists and the universities, is the most appealing call of applied science to-day. It will prove highly profitable to industry.

ACTION AND REACTION ARE EQUAL. We get out of life what we put into it. If we chemists and engineers put in much, our reward will be proportionately great; for, "Engineering is the science of directing the greatest forces of nature to the utmost benefit of man."

Spare Time—A Defense

Editor of the Journal of Industrial and Engineering Chemistry:

In the May issue of THIS JOURNAL there was published a very well-written attack upon the Editor's experiment of introducing into its pages a discussion of social industrial relations. Mr. F. O. Sprague can find in the article "no reference to chemistry, or any other science, unless it be philosophy" and on this seems to base his objections.

Now it is true that there is probably not one statement in the "Criticism" which would be successfully contradicted and yet the article as a whole shows clearly the necessity for Dr. Jordan's preaching. There are many men who take such joy in the work they are doing that they can find but very little patience to listen to anyone who does not speak on their subject. This implies an enviable sense of security in one's own chosen profession; it indicates conviction that one is on the right path of progress.

Is such an attitude justified? Has Mr. Sprague any guarantee that the highest efficiency is the highest good; does he know where we are going in this progress? I would not want to go ahead full-tilt in an unknown, dark room; I will not fix my whole attention on chemistry or shoe-cobbling to the exclusion of the art of living and the right to make more or less intelligent guesses at what this world really is. If I specialize I am more likely to further that one branch that I am paying attention to, than if I disperse my energies. But my accretions of knowledge would be rectilinear; they would have no width and I would be incapable of judging of their worth to human society. I would be a machine, working in its own special way, that would have to be started from outside, stopped from the outside, and whose product would be of value only when joined to that of other similar machines. I would be in the hands of the engineers of men the politicians, who would use my labor as they saw fit. Chemistry, instead of being a peer among peers would be a handmaid, a servant of others. Doctors and lawyers have ruled us for long, not because of the advancements in their sciences, but because for one reason and another doctors and lawyers were widely educated men, not narrowly educated. They often knew more than medicine or law, they understood human relations, they used their spare time. And it is by carpentering on the side, or by pruning rose bushes, or by long tramps through the woods, by hunting game, that you develop otherwise dormant senses and those senses, once aroused, gather for you information that would otherwise have passed you by, and give to you pleasures that make you human.

Let Mr. Sprague's philosophy of life rule; will any higher ideal then be conceivable than that of the beehive? Every bee knows its duty and attends to that alone. No bee individually is of any importance, in fact one might say that there is no meaning attached to the word "bee" and that only "bees" can be understood. Is it exhilarating to think that the time may come when this world will be a huge beehive, in which each one of us is held to one specific task, be it cobbling or chemistry, by an inexorable power, which will mete out to us rationed supplies, in quantity and quality just sufficient to keep us in our predetermined space? Does not all evidence tend to show that some such goal will most probably be ours, unless .... unless we study Social Industrial Relations besides our own chosen profession and bring a well-directed, conscious effort to bear upon future developments?

We differ, I believe it is agreed, from animals, only in that we have power over our future. Fathoming the mysteries inherent in all branches of knowledge helps us to the tools we use, but we must at the same time also learn how to use those tools and to what purpose.

Therefore I wish to record here my most emphatic vote for a continuance of such articles as Dr. Jordan's "Spare Time."

C. Dedlow

Cia. Swift de La Plata
Gran Dock La Plata, Argentine
July 15, 1921

SCIENTIFIC SOCIETIES

Adoption by the Colleges of Standard Metric Units

By Eugene C. Bingham

Chairman, Metric System Committee

In accordance with the resolution of the Council at its Rochester Meeting, we have written to the colleges and universities of the United States asking that the purchase of chemicals and supplies be made hereafter in units of the metric system. One-hundred and ninety-four colleges and universities, given in Table I, have signified by letter their intention of coöperating in this movement. Doubtless many others will join in but have failed to notify the Committee in time for this report. Only one institution, the Cincinnati College of Pharmacy, is definitely opposed to the movement so far as we have been able to learn and their reasons do not affect the general situation. It seems clear then that an overwhelming majority of the American colleges will in a short time be purchasing in metric units.

We have the written statement of twenty-seven different manufacturers and dealers (Table II) who are prepared to supply chemicals on metric specification. Several others, not on this list, are prepared to quote on metric specifications for apparatus only. It is perfectly clear that if American chemists desire chemicals and apparatus in metric units exclusively, it is only necessary to say so for the manufacturers and dealers to meet the demand. This is proved by the fact that the Eastman Kodak Co., Special Chemicals Co., National Stain & Reagent Co., U. S. Industrial Chemical Co., and the Digestive Ferments Co. already sell their products regularly on a metric basis. The Synthetical Laboratories of Chicago "are making preparations to change to the metric system as soon as containers, labels, etc., can be secured." Powers-Weightman-Rosengarten Company has just now brought out a line of analyzed chemicals put up in standard metric packages exclusively. Their catalog gives metric prices only, entirely ignoring the existence of English units. The Will Corporation "will publish by September 1, a list of chemicals and chemical apparatus in which the metric system is used." Baker & Adamson "are preparing a new price list at the present moment and have issued instructions to the effect that quotations be made in metric as well as avoirdupois units." J. T. Baker Chemical Company devote a page in their catalog of August 1921 to a very simple method for obtaining equivalent metric prices for the prices per pound or ounce, 500 g. being 10 per cent above 1 lb , etc. It is to be especially noted that the price is the same whether specifications are in pounds or grams. Several firms have plans to use their readiness to handle business in metric units as a feature in their advertising.

There is a noticeable diffidence on the part of those who are using metrics for the first time. One writes, "We are venturing to place our order this summer in metric units, probably to the annoyance of the dealer." The dealer, on the other hand, fears to "venture" until there is a strong demand for metrics from the consumer. One writes, "We are at the mercy of the customers. We need *one* system or it runs up packing charges." The president of another firm writes, "Some years ago we adopted the metric system in both the measurements of our apparatus and the weights in selling chemicals, and carried it out for about a year. At the end of this time we learned that it was impossible to force our system on our customers, * * * and that our humble efforts made very little progress in educating the country, so we went back to selling chemicals by pounds as asked for."

We are thoroughly convinced that it is necessary for the consumers to take the lead and there is every advantage in our

TABLE I—LIST OF UNIVERSITIES AND COLLEGES WHICH WILL HEREAFTER PURCHASE CHEMICALS AND CHEMICAL SUPPLIES AS FAR AS PRACTICABLE IN METRIC UNITS (PRELIMINARY)

Agnes Scott College
Alabama Polytechnic Institute
Amherst College
Anderson College
Augsburg Seminary

Bates College
Baylor University
Beloit College
Berea College
Bluffton College
Boston College
Boston University
Brenau College
Brooklyn Polytechnic Institute
Brown University
Bryn Mawr College

California Institute of Technology
Capital University
Carleton College
Carroll College
Cedarville College
Central College
Centre College
Clark College
Clemson Agricultural College
Colby College
Colgate University
College of the City of New York
College of Saint Elizabeth
Colorado College
Columbia University
Converse College
Cornell College
Cornell University

Dakota Wesleyan
Dartmouth College
De Pauw University
Detroit College of Medicine and Surgery
Drexel Institute
Drury College

Ellsworth College
Elmira College
Eureka College

Florida State College for Women
Fordham University
Franklin College
Fullerton Union High School and Junior College

George Peabody College for Teachers
Georgetown College
George Washington University
Goshen College
Goucher College
Greensboro College
Grenada College
Grove City College
Guilford College
Gustavus Adolphus College

Hanover College
Harvard College
Hastings College
Haverford College
Hibbing Junior College
Hiram College
Hobart College
Howard University

Indiana University
Indianapolis College of Pharmacy
Iowa State College

James Milliken University
Johns Hopkins University

Kentucky Wesleyan College
Kenyon College

Lafayette College
Lehigh University
Lincoln Memorial University
Louisiana State University

Macalister College
Massachusetts Agricultural College
Massachusetts College of Pharmacy
Massachusetts Institute of Technology
Medical College of Virginia
Mercer University
Miami University
Michigan Agricultural College
Michigan College of Mines
Milton College
Mississippi Agricultural and Mechanical College
Missouri Valley College
Monmouth College
Mount Union College
Municipal University of Akron

Newberry College
New Hampshire College
New Mexico College of Agriculture and Mechanic Arts
Northwestern University
Norwich University

Oberlin College
Ohio State University
Ohio University
Ohio Wesleyan University
Ottawa University

Park College
Parsons College
Pennsylvania State College
Phillips University
Princeton University
Purdue University

Reed College
Rensselaer Polytechnic Institute
Ripon College
Roanoke College
Rochester Junior College
Rutgers College

St. Bernard College
Saint Ignatius College
St. John's University
Saint Mary's College
St Olaf College
St. Xavier College
Simmons College
Smith College
So. Dakota State College and Expt. Station
So. Dakota State School of Mines
Stanford University
State College of Washington
State University of Iowa
State University of New Mexico
Swarthmore College
Syracuse University

Texas Christian University
Trinity College, N. C.
Tufts College
Tusculum College

Union College
University of Alabama
University of Arizona
University of Arkansas
University of Buffalo
University of California
University of Chicago
University of Cincinnati
University of Colorado
University of Dubuque
University of Florida
University of Idaho
University of Illinois
University of Kentucky
University of Michigan
University of Maine
University of Maryland
University of Minnesota
University of Mississippi
University of Missouri
University of Montana
University of Montana State College
University of Nevada
University of North Carolina
University of North Dakota
University of Notre Dame
University of Oregon
University of Pennsylvania
University of Pittsburgh
University of Richmond
University of Rochester
University of Santa Clara
University of South Dakota
University of the South
University of Tennessee
University of Utah
University of Vermont
University of Virginia
University of Wisconsin
University of Wyoming
Utah Agricultural College

Vassar College
Villanova College
Virginia Polytechnic Institute
Virginia Union University

Wake Forest College
Washington and Jefferson College
Washington and Lee University
Washington University
Wellesley College
Wesleyan College
Wesleyan University
Western Maryland College
Western Reserve University
West Virginia University
Wheaton College
William and Mary College
William Jewell College
Wilmington College
Worcester Polytechnic Institute

Yale University

making it unanimous and whole-hearted. There can be no serious obstacle ahead, for several of the colleges, notably Beloit, Central, Colby, Clemson, Colgate, Harvard, Iowa State, Louisiana State, Northwestern, Ohio Wesleyan, Swarthmore, Syracuse, Tufts, Union, U. of Michigan, U. of Minnesota, U. of Richmond, U. of Wisconsin, U. of Wyoming, Washington and Jefferson, Washington and Lee, and Wesleyan have for years bought chemicals and supplies either entirely or in part in metric units; and Professor F. W. Durkee says, "Our specifications for chemicals and apparatus have for many years been practically altogether in the metric system. I am surprised that this has not been the general practice of all the other institutions."

It is well to keep in mind exactly what we hope to accomplish:

(1)—We are adopting the standard unit weight already suggested by the Committee on Guaranteed Reagents and Standard Apparatus (THIS JOURNAL, 12 (1920), 1206). The quantities in the *standard packages* will normally be multiples of the *metric pound* of 500 g. In several chemicals the 100-g. package is recommended, the 200-g., 25-g., 5-g. and 1-g packages are occasionally used, but it is hoped to avoid the 250-g. and 50-g. package as being unnecessary. Chemically pure acids and ammonia will be supplied in the bottles now in use in multiples of the following:

Ammonia	2 kg.
Hydrochloric acid	2.5 kg.
Nitric acid	3 kg.
Sulfuric acid	4 kg.

TABLE II—MANUFACTURERS AND DEALERS PROFESSING READINESS TO SUPPLY THE TRADE WITH STANDARD PACKAGES OF METRIC UNITS (PRELIMINARY)

J. T. Baker Chemical Co., Easton, Pa.
Justinian Caire Co., San Francisco, Cal.
Chemical Co. of America, New York.
Denver Fire Clay Co., Denver, Col.
Dow Chemical Co., Midland, Mich.
Eastman Kodak Co., Rochester, N. Y. (Department of Synthetic Chemistry only).
Eimer and Amend, New York.
Wm. Gaertner, Chicago.
General Chemical Co. (Baker & Adamson), Easton, Pa.
Emil Greiner Co., New York.
Hercules Powder Co., Wilmington, Del.
Herrick & Voigt, New York.
Howe & French, Boston.
C. E. Ising Corporation, Flushing, N. Y.
Merck & Co., New York, St. Louis, and Montreal.
Michigan Drug Co., Detroit.
Mine and Smelter Supply Co., Denver, Col.
Miner-Edgar Co., New York.
Palo Company, New York.
Reynolds, Teschner & Volk Co., Inc., New York.
E. H. Sargent & Co., Chicago.
Special Chemicals Co., Highland Park, Ill.
Stewart & Holmes Drug Co., Seattle, Washington
Wilkens-Anderson Co., Chicago.
Will Corporation, Rochester, N. Y.
Schaar & Co., Chicago.
A. Daigger & Co., Chicago.

(2)—Exclusive use of standard units in pure chemicals will promote the best interests of manufacturer, dealer, and consumer. We shall know how to order economically, get what we order expeditiously, and the amount of stock to be carried will be reduced and repacking avoided, thus saving both time and expense. We have two systems in use. We desire only one—and that metric.

(3)—There will be greater ease in keeping laboratory inventories and accounts, chemicals and apparatus being bought from dealers and sold to students in the same units, which are also the ones we as chemists find it easiest to use.

(4)—Comparisons with European prices can be made more conveniently than heretofore. Export to foreign countries will be facilitated.

(5)—American college men will have constantly before them an illustration of the practicability of the metric system in trade. As Prof. J. N. Swan puts it, "The right way to get it into use is to use it."

(6)—The voluntary and increasing use of the metric system by the thinking men of America in the face of the general use of the English system constitutes an argument for the general adoption of the metric system which cannot be successfully controverted.

(7)—Here is an opportunity to demonstrate on a comparatively small scale whether the so-called "insuperable difficulties" of the transition period can be obviated or not. We recognize that a sudden demand for chemicals in metric units from dealers who have stock in English units only does create a problem for which we must seek a solution which will afford the minimum of inconvenience. It is for this reason that we held a conference in New York on World Standardization. We suggest that customers order from their dealers considerably in advance of actual needs so that standard packages may be obtained from the manufacturers.

We recommend that purchases be made only from dealers who will furnish materials in metric units. Customers are requested to report to the Committee the names of any dealers who refuse to furnish goods in metric packages.

Report on Standardization of Sizes and Shapes of Apparatus—I[1,2]

By W. D. Collins

Chairman, Committee on Guaranteed Reagents and Standard Apparatus

The waste of effort and money resulting from the great variety of sizes and shapes of common laboratory apparatus is generally recognized, and many laboratories have made considerable savings by standardization of equipment. The Committee on Guaranteed Reagents and Standard Apparatus in coöperation with the Committee on Standardization of the Association of Scientific Apparatus Makers is attempting to extend the benefits of such standardization to all members of the American Chemical Society. The Committee of the Apparatus Makers Association has furnished data on sales of certain items and has obtained recommendations from representative dealers in regard to all the items considered. The modifications of these recommendations by the Committee on Guaranteed Reagents and Standard Apparatus have been in retention of articles which are necessary although purchased only in small quantities, and in omission of items which the Committee felt should not be used, although probably many sales were made to purchasers who kept on buying something they had always used although they could do better work with newer apparatus.

The recommendations are made with reference to having the articles listed in dealers' catalogs and kept in stock for immediate delivery. If dealers and manufacturers adopt the recommendations some articles which can be manufactured commercially only in large quantities may be difficult to obtain, while others which are made by hand can be obtained almost as easily as at present.

The articles considered by the Committees include all of the common types carried by the apparatus supply houses and detailed descriptions of them may be found by reference to any complete catalog of chemical apparatus.

The articles are listed under three classifications:

1—Lists in which only the *discontinued* items are given—all other items under these headings are retained.

2—Lists in which only the *retained* items are given—all other items under these headings are discontinued.

3—Lists in which both the *retained* and *discontinued* items are given.

Absorption Bulbs for Solid Reagents

Discontinue

Wesson's for absorption of CO_2

Adapters

Discontinue

Straight, 250 mm. × 35 mm.
Bent at 45° angle, 250 mm. × 35 mm.

Alkalimeters

Discontinue

Geissler's carbon dioxide apparatus, new form with ground joints
Knorr's carbon dioxide apparatus, with rubber connections

Burets

It was recommended that all burets be graduated as follows: 10-cc. burets in 1/20-cc. divisions; 25-cc. burets in 1/10-cc. divisions; 50-cc. burets in 1/10-cc. divisions; 100-cc. burets in 1/5-cc. divisions

Discontinue

For pinchcock, 10-cc. capacity
For pinchcock with side tube, all sizes
With straight glass stopcock and side tube, all sizes
With three-way stopcock, 100-cc. capacity
With Fresenius stopcock, 25-cc. capacity
With Fresenius stopcock and side tube with glass stopcock, 25-cc. capacity
Gawalowski, straight glass stopcock, and side tube with glass stopcock, all sizes
Schellbach, for pinchcock, with side tube, all sizes
Schellbach, with three-way stopcock, 25-cc. capacity
Dispensing, for pinchcock, all sizes

Burners

Discontinue

Bunsen, with stopcock on gas inlet tube; ordinary
Bunsen, central draft, without air regulator
Bunsen, central draft, for use with gasoline gas, without air regulator
Bunsen, micro form, 3 in. high, large size
Argand, adjustable, copper chimney, 7 in. high
Argand, glass chimney, 7 in. high
Koch safety, 6-in. height, large size
Koch safety, small size, on stand, both sizes
Koch safety, large size, on stand, without regulator
Koch safety, two burners on stand, with weight release
Mica chimney only with clamp for Koch safety burner
Méker, for artificial gas, No. 0 size
Méker, for natural or gasoline gas, No. 0 size
Multiple tube, ordinary, with 2 tubes on same base
Multiple tube, ordinary, 3 tubes in circle
Multiple tube, ordinary, 4 tubes in circle
Multiple tube, ordinary, 6 tubes in circle
Multiple tube, ordinary, 4 tubes in row
Multiple tube, ordinary, 4 tubes in row, with stopcock
Fletcher's Argand, all sizes
Fletcher's evaporating, solid copper, sizes B and C
Fletcher's low temperature, with blast pipe
Fletcher's radial, for gasoline gas, all sizes
Fletcher's solid flame for gasoline gas
Gas stove, round, 9 in. diameter, on feet, for gasoline gas
Gas stove, burner only, on legs, with dish supports
Glass blowers' fires, with horizontal air and gas inlet pipe
Glass blowers' fires, with vertical air and gas inlet pipe to go through table
Burner tip for glass blowers' fires
Illuminating, with Welsbach burner, on round base
Ring form, with regulator, 5 in. diameter
Roger's ring
Soldering iron heater, for gas
Soldering iron heater, for gasoline gas

---

[1] Supplementary to the report published in This Journal, 13 (1921), 402.

[2] Prepared by the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society in collaboration with the Committee on Standardization of the Association of Scientific Apparatus Makers of the United States of America.

Soldering iron heater, for natural gas

Bunsen, with adjustment for air and gas

Boyce's Acme safety

Boyce's adjustable

Detroit adjustable

Teclu's, all sizes

High temperature, with straight tube and enlarged top with drilled solid grid, all sizes

High temperature, same as above, with four burners in row

Blast, Fletcher's injector, all sizes

Blast, Méker, with air inlet tube, for coal gas only, all sizes

Blast, Wiesnegg, with stopcocks

Alcohol lamp, of glass, jeweler's type, can be placed in inclined position

Wicks for alcohol lamp

Barthel's alcohol stove, with attached reservoir, double burner

Alcohol blast, double jet

Alcohol stove, ring burner with dish supports

Burner tube for gasoline torch, brass

Tip nut for gasoline torch, brass

Blast lamp only for adjustable laboratory blast lamp, plumber's torch on swivel stand with dish holder

Stand, only for above-mentioned burner

Repair parts, only for laboratory blast lamp burner, plumber's torch; and for adjustable laboratory blast lamp burner, plumber's torch on swivel stand with dish holder

Burner chimneys with attached support, all sizes

Burner tripods, or dish supports for attachment to Bunsen burners, for burner tube ½ in. diameter

Calcium Chloride Tubes

Retain

Straight, one bulb

Cat. spec. Mm.	Length over-all Mm.	Length to bottom of bulb Mm.	Inner diam. tube Mm.	Diam. bulb Mm.	Length of stem Mm.	Diam. of stem Mm.
100	140	100	14	25	40	6
150	190	150	16	30	40	6
200	240	200	18	32	40	6

Straight, two bulbs

Cat. spec. Mm.	Length over-all Mm.	Length to bottom of 1st bulb Mm.	Inner diam. tube Mm.	Diam. top bulb Mm.	Length of stem Mm.	Diam. of stem Mm.
100	155	100	14	25	30	6
150	205	150	16	30	30	6
200	255	200	18	32	30	6

U shape, plain

Cat. spec. Mm.	Length over-all Mm.	Inner diam. tube Mm.
100	100	14
150	150	16
200	200	18

U shape, with side arms

Cat. spec. Mm.	Length over-all Mm.	Inner diam. tube Mm.	Length side arm Mm.	Diam. side arm Mm.	Dist. below top Mm.
100	100	14	40	6	20
150	150	16	40	6	25
200	200	18	40	7	30

Schwartz, with side tubes and ground glass stoppers

Cat. spec. Mm.	Length over-all w/t stop. Mm.	Inner diam. tube Mm.	Length side tube Mm.	Outside diam. side tubes Mm.
100	100	15	40	6
150	150	15	40	6

Straight with two bulbs, smaller having inner tube to trap moisture, 100 mm., 150 mm.

Volhard's U-tube with side arms, one arm having a bulb to collect moisture, 100 mm., 150 mm.

Marchand's U-tube with permanent side tube, 150 mm.

Peligot's U-tube with 3 bulbs, 100 mm., 150 mm.

Drying towers, for cork connections, 250 mm., 300 mm.

Drying towers, with ground stopcock, stopper, and connections for rubber tubing, 250 mm., 300 mm.

Condensers

Retain

Allihn's, with adapter sealed on, 200 mm., 300 mm., 400 mm., and 600 mm.

Hopkins, total length 380 mm.

Liebig's, rubber connections, and adapter, 300 mm., 400 mm., 500 mm., 600 mm., 750 mm.

Liebig's, permanent seal, with adapter, 250 mm., 300 mm., 400 mm., 500 mm., 600 mm.

Liebig's, coiled condenser tube, with adapter, 200 mm., 300 mm., 400 mm., 600 mm.

Distilling Tubes

Discontinue

With vapor inlet tube

Knight's

Le Bel-Henniger's, 2 bulb, 4 bulb, and 5 bulb

Wurtz's with two bulbs

Young's with 15 discs

Flasks, Miscellaneous

Discontinue

Erlenmeyer, ground glass stopper, resistance, 60 cc. and 1000 cc.

Assay beaker, resistance glass, 1000-cc. size

Copper, heavy, with ring neck, 250 cc. and 2000 cc.

Copper oxide, ground glass stopper, all sizes

Distilling, Claissen's, angle 75°, 3 in. immersion, 10 cc., 60 cc., 2000 cc.

Distilling, Ladenburg, 3 bulbs, all sizes

Distilling, Ladenburg, Pyrex glass, all sizes

Distilling, 3 necks, Pyrex glass, all sizes

Distilling, Lunge, with trap, all sizes

Elutriating, Benningsen, 400-cc. capacity

Extraction, resistance grade, flat bottom, wide mouth, vial neck, 60-cc. size

Extraction, round bottom, Pyrex glass, all sizes

Filtering, Erlenmeyer form, heavy glass, side neck, 750 cc.

Filtering, glass stopcock on side neck, 250 cc. and 2000 cc.

Filtering, side tube, funnel ground in neck, all sizes

Gray's carbon residue, opaque fused silica, 50 cc.

Joliet, for use in analysis of iron and steel, all sizes

Kjeldahl, round bottom, long neck, resistance glass

Kjeldahl, flat bottom, and long neck, all sizes

Kjeldahl, round bottom, short neck, 500 cc.

Melting point and oxygen, Pyrex glass, long neck, all sizes

Moisture, copper, single wall, 1000 cc.

Phosphorus, Erlenmeyer, narrow neck, resistance, 400 cc.

Distilling, Tuttle, glass stopper, 1500 cc.

Distilling, Anschutz, all sizes

Distilling, Hempel, bent side tube, Pyrex

Filtering, pear shape, side neck, heavy glass, all sizes

Generating, thistle tube and delivery tube, all sizes

Sulfur, Pyrex, Erlenmeyer, 500 cc.

Sulfur, flat bottom, side neck, vial neck, all sizes

Johnson's sulfur, Pyrex glass, 275 cc.

Volumetric, 20 cc. and 300 cc.

Volumetric, with glass stopper ground in, 20 cc. and 300 cc.

Volumetric, conical shape, enlarged mouth, capacity 100 cc.

Volumetric, according to the requirements of the Bureau of Standards, Pyrex, Sugar, Bates', pear shape, 100 cc.

Shaking, unstoppered, heavy glass, graduated, all sizes

Shaking, glass stoppered, heavy glass, graduated, all sizes

Volumetric, graduated neck

Porcelain (D = Discontinue; R = Retain)

Beakers, without lip

Sizes:	1	1a	2	3	3a	4	5	6
	D	D	R	R	R	R	D	D

Beakers, with lip: D—all sizes

Beakers, dye pots, without lip

Sizes:	2	3	4
	R	R	R

Beakers, Griffin, with lip: D—all sizes

Beakers, dye pots, heavy flange and handle socket

Sizes:	2	3
	R	R

Beakers, dye pots, without lip, with heavy flange: D—all sizes

Beakers, dye pots, without lip, with support flange, high form: D—all sizes

Boats, combustion, glazed

Sizes:	0	1	2	3	4	5	6	6a	7	8
	D	R	R	D	D	D	R	R	D	R

Boats, combustion, unglazed: D—all sizes

Capsules, without lip, round bottom: D—all sizes

Capsules, without lip, straight sides, flat bottom

Sizes:	1	3	4
	R	R	D

Capsules, combustion, without lip, round bottom

Sizes:	3	4
	R	R

Casseroles, with handle

Sizes:	1	2	3	3a	4	4a	5	6	7
	D	R	R	R	R	R	R	R	D

Casseroles, with extra long handle: D—all sizes

Cones, filter

Sizes:	3	4
	R	D

Crucibles, high form

Sizes:	000	00	0	1	1a	2	3	4	5
	D	R	R	R	D	R	D	D	D

Crucible covers, for above

Sizes:	000	00	0	1	1a	2	3	4	5
	D	R	R	R	D	R	D	D	D

Crucibles, low form

Sizes	0000	000	00	0	1	2	3	4	5
	D	R	R	R	R	R	R	R	R

Crucible covers, for above

Sizes:	0000	000	00	0	1	2	3	4	5
	D	R	R	R	R	R	R	R	R

Crucibles, Gooch

Sizes:	2	2a	3	4
	R	D	R	R

Crucible covers, for above

Sizes:	2	2a	3	4
	R	D	R	R

Crucibles, Gooch, for extraction apparatus

Sizes:	2	3
	D	R

Crucibles, Gooch, straight sides

Sizes:	1	3
	D	D

Crucible covers, for above

Sizes:	1	3
	D	D

Crucibles, Rose

Sizes:	1	2	3
	R	R	D

Crucible covers, for above

Sizes:	1	2	3
	R	R	D

Delivery tubes, for above

Sizes:	1	2	3
	R	R	D

Crucible, bitumen

Size:	2
	R

Crucible, Caldwell

Sizes:	1	3
	D	R

Crucible covers, for above

Sizes:	1	3
	D	R

Disks, perforated

Sizes:	1	2	3	4	5	6	7	8	9	10	11
	R	R	R	R	R	R	R	R	D	D	D

Crucibles, cylindrical: D—all sizes

Crucibles, glass pot: D—all sizes

Cups, annealing

Size:	0
	R

Cups, swimming

Sizes:	1	2
	D	D

Evaporating dishes, with lip

Sizes:	000	00	New Size Diam. 75 mm. Cap. 70 cc.	0	1	2	3
	R	D	R	D	D	R	R

4	New Size Diam. 115 mm. Cap. 250 cc.	5	6	6a	7	8
D	R	D	R	D	D	R

8a	9	10	11*	12*	13*
D	R	D	R	R	R

*Sizes 11, 12, and 13 to have welter rim

Dishes, evaporating, with heavy welter rim: D—all sizes

Dishes, evaporating, shallow form: D—all sizes

Dishes, crystallizing, with lip: D—all sizes

Dishes, crystallizing, without lip: D—all sizes

Funnels, Büchner

Sizes:	0	1	2	2a	3	4	4a	5
	R	R	R	R	R	R	R	R

Funnels, Hirsch

Sizes:	0000	000	00	0	1	2	3	4
	R	R	R	R	R	D	D	D

Mortars and pestles

Sizes	55 mm.	80 mm.	100 mm.	130 mm.	150 mm.	185 mm.
	R	R	R	R	R	R

213 mm.	260 mm.
R	R

Mortars and pestles, deep form: D—all sizes

Plates, color

Sizes:	1	2	3	4
	R	D	D	D

Plates, flat: D—all sizes

Plates, desiccator, with 3 small feet

Sizes:	0	1	2	2a	2b	3	4	5
	D	R	R	D	D	R	D	D

Plates, desiccator, without feet

Sizes:	4	5
	R	R

Plates, desiccator, with numerous 5mm. holes

Sizes:	4	5
	R	R

Plates, streak

Sizes:	1	2	3	4	5	6
	D	D	D	D	R	D

Porous plates, round: D—all sizes

Porous plates, square: D—all sizes

Porous plates, dinner plate shape

Sizes:	1	2
	D	R

Spatulas, with knob on one end

Sizes:	1	2	3	4	5	5a	6
	D	D	R	D	R	D	R

Spatulas, both ends

Sizes:	1	2	3	4	5	5a	6	7
	D	R	R	R	D	D	D	D

Spatulas, one end spoon

Sizes:	1	1a	2	3	4	4a	5	6
	R	R	R	R	D	D	D	D

POTASH BULBS

Discontinue

- Bender and Hobein
- Bowen, large size
- Geissler, with drying tube sealed on
- Liebig-Dittmar with trap
- Liebig-Kyll, constructed on stand
- Mitscherlich
- Winkler, spiral form, 180 mm. size
- Winkler-Kyll, spiral around conical center
- Zahradink, with ground-on drying tube

PYREX GLASSWARE

Griffin beakers, lipped

Sizes:	30 cc.	50 cc.	100 cc.	150 cc.	250 cc.
	D	R	R	R	R
	400 cc.	600 cc.	800 cc.	1000 cc.	1300 cc.
	R	R	R	R	D
	1500 cc.	2000 cc.	2500 cc.	3000 cc.	4000 cc.
	R	R	D	R	R

Berzelius beakers, lipped

Sizes:	100 cc.	150 cc.	200 cc.	300 cc.	400 cc.
	D	D	D	D	D
	500 cc.	600 cc.	800 cc.	1000 cc.	
	D	D	D	D	

Griffin beakers, no lip

Sizes:	30 cc.	50 cc.	100 cc.	150 cc.	250 cc.
	D	D	D	D	D
	400 cc.	600 cc.	800 cc.	1000 cc.	1300 cc.
	D	D	D	D	D
	1500 cc.	2000 cc.	2500 cc.	3000 cc.	4000 cc.
	D	D	D	D	D

Berzelius beakers, no lip

Sizes:	100 cc.	150 cc.	200 cc.	300 cc.	400 cc.
	R	D	R	R	R
	500 cc.	600 cc.	800 cc.	1000 cc.	
	R	D	D	D	

Boiling flasks, flat bottom, vial mouth

Sizes:	50 cc.	100 cc.	New Size 125 cc.	150 cc.	200 cc.
	R	D	R	D	D
	New Size 250 cc.	300 cc.	400 cc.	500 cc.	700 cc.
	R	D	D	R	D
	1000 cc.	1500 cc.	2000 cc.	3000 cc.	6000 cc.
	R	D	R	R	R
	12000 cc. No. 10 Stop.	12000 cc. No. 13 Stop.	24000 cc.		
	D	R	D		

Boiling flasks, flat bottom, ring neck

Sizes:	500 cc.	700 cc.	1000 cc.	1500 cc.	2000 cc.
	R	D	R	D	R
	3000 cc.	6000 cc.			
	R	R			

Boiling flasks, round bottom, vial mouth

Sizes:	100 cc.	150 cc.	200 cc.	300 cc.	400 cc.
	R	D	R	R	D
	500 cc.	700 cc.	1000 cc.	1500 cc.	2000 cc.
	R	D	R	D	R
	3000 cc.				
	D				

Erlenmeyer flasks, narrow mouth

Sizes:	25 cc.	50 cc.	100 cc.	New Size 125 cc.	150 cc.
	D	R	D	R	D
	200 cc.	New Size 250 cc.	300 cc.	500 cc.	600 cc.
	R	R	D	R	D
	750 cc.	1000 cc.	1500 cc.	2000 cc.	3000 cc.
	D	R	D	R	R
	4000 cc.	6000 cc.			
	R	R			

Erlenmeyer flasks, wide mouth

Sizes:	250 cc.	500 cc.	750 cc.	1000 cc.	2000 cc.
	R	R	D	D	D

Filtering flasks, with tubulature

Sizes:	250 cc.	500 cc.	1000 cc.	2000 cc.	4000 cc.
	R	R	R	R	R

Filtering flasks, no tubulature

Sizes:	250 cc.	500 cc.	1000 cc.	2000 cc.	4000 cc.
	D	D	D	D	D

Flasks, round bottom, short ring neck

Sizes:	200 cc.	500 cc.	1000 cc.	1500 cc.	2000 cc.
	R	R	R	D	R
	3000 cc.	5000 cc.	12000 cc.		
	R	R	R		

Balloon flasks, ring neck

Sizes:	22 liter	50 liter	75 liter
	R	R	R

Balloon flask, without ring neck

Size:	75 liter
	D

Kjeldahl flasks, round bottom, long neck

Sizes:	300 cc.	500 cc.	650 cc.	800 cc.
	R	R	D	R

Extraction flasks, flat bottom, vial mouth

Sizes:	50 cc.	100 cc.	150 cc.	250 cc.	500 cc.
	R	R	R	R	R
	750 cc	1000 cc.	2000 cc.	3000 cc.	
	R	D	D	D	

WOODEN SUPPORTS (D = Discontinue; R = Retain)

(R) 1—Separatory funnel, as illustrated in Leach

(R) 2—Funnel, for 6 funnels in row, adjustable in height, holes slotted to facilitate removal of funnels

(D) 3—Funnel, same as above, but for 12 funnels in row

(D) 4—Funnel, similar to above, for 12 funnels in two rows, adjustable to 16½ in. in height

(D) 5—Funnel, old form, similar to (2) but 6 funnels in one row; holes not slotted

(D) 6—Funnel, similar to (4) but for 6 funnels in one row, and holes not slotted

(R) 7—Funnel, with double arm for 4 funnels on center support rod, with holes slotted to facilitate removal of funnels

(D) 8—Funnel, for 4 funnels, same as (7) but with holes not slotted

(D) 9—Funnel, same as (8) but for 2 funnels

(D) 10—Funnel, single arm, for 2 funnels, holes not slotted

(D) 11—Funnel, same as (10), for 1 funnel

(R) 12—Funnel, single arm, for 1 funnel, arm broadened to provide beaker support

(R) 13—Universal, Gay-Lussac's, for tubes or rods

(R) 14—Universal, Schellbach, with swivel joint for rods or tubes

(R) 15—Universal, with right angle clamp and long extension rod

(D) 16—Buret, for 1 buret

(R) 17—Buret, double arm, for 2 burets

(D) 18—Buret, same as above, with steadying arm, for 2 burets

(D) 19—Buret, similar to (16) but with one jaw hinged

(R) 20—Buret, similar to (17), with hinged jaws, for 2 burets

(D) 21—Buret, same as (20), but with steadying arm, for 2 burets

(D) 22—Buret, same as (17) but for 4 burets

(D) 23—Support table, with leaded base and round top; height 10 in. and can be extended to 15 in.

(R) 24—Pipet, revolving, for 12 pipets

(D) 25—Buret holder for 2 burets, for attachment to reagent shelf; hinged to permit swinging upward out of way when not in use

(D) 26—X-ray tube floor stand with swivel joint on tube clamp and also on support rod

(D) 27—X-ray tube floor stand, similar to above, but without swivel on tube clamp

(D) 28—Tube holder only for (26)

(D) 29—Tube holder only for (27)

(D) 30—Support for 18 test tubes in 2 tiers; holes for 2 funnels; with drying pins

(D) 31—Test tube, knocked down, for 16 tubes in 2 tiers, with drying pins

(R) 32—Test tube, knocked down, for 25 tubes in 2 tiers, with drying pins

(D) 33—Test tube, same as (32), for 25 tubes in 2 tiers but cannot be knocked down with drying pins

(D) 34—Test tube, same as (33) but for 16 tubes in 2 tiers, with drying pins

(R) 35—Test tube, same as (34) but for 13 tubes in 2 tiers, with drying pins

(R) 36—Test tube, for 12 one-inch tubes in two rows, with 12 drying pins

(R) 37—Test tube, for 12 one-inch tubes in 2 rows, without drying pins

(R) 38—Test tube, for 12 tubes, same as (37) but for tubes up to $^7/_8$ in.

(D) 39—Test tube, for 12 tubes, same as (38) but for tubes up to $^3/_4$ in.

(D) 40—Test tube, for 12 tubes in single row, with 12 drying pins

(D) 41—Test tube, for 10 tubes in single row, with 10 drying pins

(R) 42—Test tube, 6 tubes in single row, with 6 drying pins

(D) 43—Test tube, same as above but for 4 tubes, with 4 drying pins

(D) 44—Test tube, for 24 Wassermann tubes up to ½ in. in 2 rows; without drying pins

(R) 45—Test tube, Griffith type, for 10 tubes up to $^7/_8$ in. and 2 tubes up to $1^1/_8$ in.; with 12 drying pins and drain groove

(R) 46—Test tube, for 24 tubes up to $^3/_4$ in. in 2 rows; without drying pins

(D) 47—Test tube, similar to (42) but for 12 tubes in 2 rows, with 6 drying pins and drain groove

(R) 48—Test tube, drying rack, for drying test tubes or flasks, 50 drying pins

(R) 49—Test tube, same as (48) but with 25 drying pins

(R) 50—Clamps, flask, for flasks and large tubes, wood, with spring

(R) 51—Clamps, test tube, wood, with wire spring

WEIGHING BOTTLES

Retain

Conical form, with flat bottom and ground glass stopper, capacities 15 cc., 30 cc., and 60 cc.

High form, flat bottom, ground stopper, without neck, sizes

	Mm.	Mm.	Mm.
Height:	60	80	100
Diameter:	15	15	25

Low form, flat bottom, ground glass stopper, without neck, sizes:

	Mm.	Mm.	Mm.
Height:	50	50	60
Diameter:	25	40	30

Extra wide form, flat bottom, without neck, ground glass stopper, sizes:

	Mm.	Mm.	Mm.
Height:	30	30	30
Diameter:	60	60	70

Parr's, with cover ground outside

Grethen's form, with glass stopcock, weighing pipet, capacity 2 cc.

Lunge's weighing pipet, with two stopcocks, capacity 15 cc.

Apparatus for Miscellaneous Liquid Reagents

Discontinue

Absorption tube, Babo's, filled with glass beads
Absorption tube, Camp's, 330 mm. over all, 27 mm. diameter with stopcock
Absorption tube, Hinman's, used for the determination of ammonia in gas
Absorption tube, Meyer's, for absorption of carbon dioxide
Ammonia absorption apparatus, Cumming's, for determination of ammonia in gas
Ammonia absorption apparatus, Referee's, filled with glass beads
Fresenius nitrogen bulb
Volhard's nitrogen bulb
Volhard's latest form nitrogen bulb
Nitrogen bulb, Will-Varrentrap's, with 3 bulbs
Nitrogen bulb, Will-Varrentrap's, with 4 bulbs
Sulfur apparatus, Meyer's, for absorption of sulfur, with 6 bulbs
Sulfur apparatus, Meyer's tube, same as above but with ground stopper, stopcock, with 6 bulbs

---

The Meeting of the Section of Chemical Education

While the Section of Chemical Education is one of the most recent sections of the American Chemical Society its sessions at the New York Meeting more than made up in interest, enthusiasm, and attendance for its extreme youth. It may have been due to its good fortune in having for its presiding officer that genial and versatile Nestor of American Chemical Education, President Edgar F. Smith, or to inherent interest in the subject of chemical education, or to both of these, but certain it is that those who came early to attend the sessions stayed to the end, while those who came late generally found standing room only.

President Smith gave ample time for presentation of papers and then encouraged discussion, in which those in attendance seemed always ready to participate. The program had been admirably arranged to cover some of the most important questions which have arisen in connection with the teaching of chemistry. Considerable difference of opinion developed during the discussions and no definite conclusions were reached or formally agreed upon which can be stated as the result of the discussions, but that was hardly to be expected. In a good many cases, however, it was quite obvious from the discussion what the general opinion of those present was on some very important questions. The Section will no doubt be made permanent and we may expect more tangible results in the future along the line of agreement on fundamental principles for teaching chemistry.

At the first session, held Wednesday afternoon, President Smith stated the purposes and aims of the Section to be a study of the methods and objects of Chemical Education.

The first formal paper was read by Prof. David Snedden of Teachers College, Columbia University. Prof. Snedden started out with the assumption that the present condition of the instruction in chemistry, as well as that of other science subjects in school and college, is in a very low state and that it is urgently necessary to find some remedy for the present bad situation.

He suggested that the remedy might be found in a division of students of chemistry into two groups, one of which would include those who desired to study chemistry as a cultural subject, while the other included those who expected to follow vocations in which chemistry is of vital importance, such as farming, homemaking, mining, engineering, pharmacy, etc. Professor Snedden held that the elements of the hard or systematic chemistry need not be taught to the first group but that their needs would be met by a so-called informational course. He stated that it was becoming increasingly difficult to exact from students even of the second group the same intensive study of fundamentals which characterized student habits of a former generation. He asserted that even serious study of mathematics might soon be out of the question on account of the modern spirit which induces students to ask to be shown the utility of it all. Professor Snedden held that students and practitioners of chemistry were bad guides as to standards in teaching chemistry.

The animated discussion which followed indicated that those in attendance were opposed to the views presented. The large number of failures in Freshman classes was attributed to the laxity in instruction in secondary schools. It was pointed out that it would be impossible to give adequate professional instruction to high school graduates who had not been given thorough courses in preparatory subjects. The constantly increasing attendance at high schools includes many young people who are not serious students and cannot carry college courses, but such students should not be allowed to determine standards for those desiring to attend college which will result in their failure later.

The situation was stated as follows by Prof. A. W. Smith of the Case School of Applied Science:

> My criticism of the position of the high school administrators is that the whole tendency is to make the work of the high school student easy and irresponsible. The general observation of college instructors for some years past is that the high school graduates are unable to apply themselves to real work. It takes from two to three years of the college course to teach these students how to work properly. The great proportion of men dropped from college is largely due to this fact.
>
> The statement has been made that high school students could not be made to take any course that was difficult or of which they did not perceive the utility. This statement appears to sound so foolish that it should not be necessary to discuss it further. The idea that a high school boy is competent to select studies that will be for his best advantage in the long run seems absurd. The idea that high school students cannot be required to take courses that are difficult in order to learn to apply themselves properly indicates that some different management of the high schools is desirable. If a boy of fifteen or sixteen cannot be controlled by teachers or authorities, it is time other authorities were selected who could control such boys.

President Smith closed this discussion by remarking that in his young days his father would have been apt to say that if he could not carry his Freshman courses without getting conditioned he had better return to the farm.

Papers on the general subject of the chemistry to be taught during the first and second year of the college course were read by Professors William McPherson, H. N. Holmes, Lyman C. Newell, and Herbert F. Davison.

It seemed to be the general practice to divide college freshmen into two groups according to whether the student had or had not had chemistry in the high school. The instruction to these groups is carried out in most colleges in different classes and differs considerably in character, although the general practice seems to be to present to each group the facts and principles of general chemistry. The papers read brought out considerable differences in practice in the subject matter of the course given to the group which had had high school chemistry, the extremes being a short course in advanced general chemistry followed by qualitative analysis in the Freshman year on the one hand, and, on the other, extending the instruction in general chemistry into the Sophomore year. The necessity of making the course for the group which had had high school chemistry distinctly different as to scope, textbook and laboratory work was strongly emphasized.

The character of the laboratory work prescribed for this group in one university was given in one of the papers presented. The experiments consisted mainly of quantitative determination of fundamental values in chemistry, such as molecular and atomic weights, solubilities, densities of gases, and elementary experiments in physical chemistry, such as speed of reactions, conductivities, mass action, fractional distillation, etc.

On Thursday morning the sessions were resumed in a larger room in the Journalism building.

A paper entitled "Systematic Care of Chemistry Students" was read by Prof. Alexander Silverman of the University of Pittsburgh. This paper gave in the most exact detail methods in use for determining student grades, purchase of supplies, procedure in recitations, lectures, and laboratory and conference with students.

The method of grading students aroused the most interest. Professor Silverman advocated a system by which laboratory work, recitations and examinations should be carefully graded, record sheets to be filled out monthly with all grades. He advised that the student be informed of all grades and be given opportunity to interview instructors with respect to grades he considered incorrect.

From the discussion which developed on this subject it appeared that an elaborate system of grading was not in general use and that many of those present did not consider such a system advisable or desirable. Other methods presented in the paper seemed to meet with general approval.

The remainder of the morning's program was devoted to a symposium on "Fostering the Spirit of Research in Colleges and Universities." President Smith was scheduled for a paper on "What Is Meant by the Spirit of Research" but insisted on hearing the other papers first and at the close of the session declared that it was unnecessary for him to deliver this paper.

Prof. Edward Ellery of Union College, Schenectady, N. Y., read the first paper on "Teaching the Elements of Research." Professor Ellery presented the results of an experiment being conducted at Union College which is a radical departure from the ordinary college methods of instruction. To a large extent the "class" scheme of instruction is abandoned. The students are divided into small groups which meet daily with an instructor in what may be called a seminar. The student is encouraged early in his course to use the library, the large treatises, and the periodicals in gaining information on problems presented to him and in which he is interested. A great deal of the student's time is also spent in the laboratory carrying out the usual experiments in the various branches in chemistry, with the exception that he is encouraged in each course to carry out experiments not found in the ordinary texts. The indifferent and mechanical student is eliminated from the school as early as "one can be certain that the spirit of research is not in him, either latent or dormant. The elimination can ordinarily take place safely at the close of the second year."

In the Junior year physical chemistry is taught by means of lectures, a seminar, and laboratory practice. During the Senior year work is begun and pursued on an original problem. The aim of the course is to prepare young men for a research career in a university or an industry. It is not calculated to expand the limits of chemical knowledge in any large or important respect.

Professor Ellery stated that this method of teaching chemistry had not been tried out long enough to enable those in charge to observe the success attained by the graduates but that the results which had been observed were so favorable that the experiment would be continued.

It was obvious to all who heard the paper and the discussion that followed that this method of instruction could not be applied to large classes unless a very large teaching staff were employed, also that it was the exact antithesis of methods employed in so many schools, by which the student is required to learn a carefully outlined set of facts and principles and given as nearly as possible mathematically exact rating on the amount of knowledge which he has absorbed. It seemed to most of those present that the best method of teaching must be somewhere in the golden mean between these extremes.

Reports were next heard from several institutions as to the methods and extent to which research was carried on at their respective institutions. Dr. W. A. Noyes reported on conditions at the University of Illinois and Prof. H. P. Talbot on conditions at the Massachusetts Institute of Technology. Professor Talbot emphasized especially the opportunity offered at M. I. T. for carrying on research in technical processes in the School of Chemical Engineering Practice in coöperation with a number of associated industries where stations had been located.

Prof. J. C. Olsen of the Polytechnic Institute of Brooklyn emphasized the importance of stimulating the spirit of research in the student in every chemical course which is presented. The student should be encouraged to make his own observations and neither the printed directions for the laboratory work nor the instructor should give in advance to the student the result to be expected, thus robbing the student of the pleasure and mental stimulus of making his own observations and conclusions.

A sufficient amount of laboratory work should be offered in all courses so that the student is given some opportunity for choice of experiments, so that he may work on experiments which interest him. The passing grade in a given subject should be given on the basis of proficiency and thorough understanding of work accomplished and not on the basis of a fixed number of experiments performed. Students should be given particular credit for interest and skill shown in trying out or developing new laboratory methods, particularly in the more advanced courses.

There seemed to be general agreement among those present on the desirability and general practice of assigning a subject for investigation to the student in his last year, a considerable part of the time of the fourth year being given to this problem. A criticism of the method of assigning and carrying out the work on such a problem was made by Prof. James F. Norris. He referred to the practice of some professors of using students to do the work on problems preparatory to the publication of a paper, all details of the work being specified by the professor, the student not being allowed to work out his salvation on his own initiative or in his own way. Very little benefit results to the student from such work. While the professor should make suggestions to the student and warn him of gross errors, the student should be allowed to learn by making mistakes and should also be given the credit if a method, questioned by the professor, results successfully.

A symposium on the question "Is the Average College Graduate in Chemistry Capable of Taking up Research?" was participated in by Drs. W. R. Whitney, M. L. Crossley, W. J. Hale, J. M. Weiss, H. D. Gibbs, and B. F. Lovelace. The general conclusion was that the average college graduate needed considerable additional guidance and instruction before he was capable of independently carrying on successful scientific or industrial research. Dr. Lovelace stated that it had been found necessary at the Johns Hopkins University to give the average college graduate at least one and one-half years' academic training before he was prepared to undertake research.

Dr. Thomas B. Freas read a paper on the "Most Efficient Equipment for a Laboratory," discussing not only the character of the apparatus but also methods of operating the chemistry stores and care of equipment.

Prof. Neil E. Gordon read a paper on "When Will the Teaching of Chemistry Become a Science" which seemed very timely in view of the great diversity of opinion and practice which had been brought out at the meeting.

Prof. Harrison Hale read a paper on "American in Teaching Chemistry" in which he pointed out the many important contributions to chemical science and industry which had been made in America, the magnitude of American resources, the fundamental importance of chemistry to America and American responsibility and opportunity. Professor Hale pointed out the considerable amount of literature which is being developed along these lines as well as the increasing number of chemical articles being published in current magazines and newspapers.

THE "HISTORY OF CHEMISTRY" MEETING

Upon concluding the program, the members adjourned to attend the symposium on the "History of Chemistry." This proved to be most interesting, on account of the many rare portraits, books, letters, and pamphlets which were shown.

President Edgar F. Smith started the symposium in a most interesting talk on Joseph Priestley and the benefits derived from a study of the history of our own American chemists. Many old books on chemistry were shown, together with a very rare letter written and signed by Priestley himself.

Dr. Ernst Cohen, of the University of Utrecht, spoke of the history of chemistry as taught in the Dutch universities.

Dr. Lyman C. Newell, of Boston University, explained methods in use for the preservation of letters and documents which would be otherwise destroyed by handling. He showed old letters fastened between sheets of celluloid to facilitate handling and protect the letters effectively. He discussed methods of collecting portraits and old books, and their use in the teaching of the history of chemistry. Signed letters of Davy, Dalton, Faraday, Lavoisier, and Mendeleeff were shown, together with some rare old pamphlets and books.

Dr. C. A. Browne, of New York City, gave a very interesting talk on the alchemists of New England. Many of those present did not know that there ever had been any alchemists in New England. Many copies of letters and documents of these alchemists were shown, and also what was thought to be one of the oldest bills for chemicals now in existence.

Dr. Goldsmith discussed a visit to Priestley's home at Northumberland, Pa., while Prof. H. G. Byers, of Cooper Union, gave a number of interesting incidents from the early history of chemistry.

Dr. Charles A. Doremus, of New York City, spoke of the work of Dr. John W. Draper, who was noted for being the first to make an image of the human face.

Dr. Adolph, of Shantung Christian College, gave a very interesting account of chemistry among the Chinese, while Prof. K. C. Pandya, of India, discussed the Hindu's contribution to chemistry, both ancient and modern.

The opinion was expressed by one professor of chemistry who attended all the sessions that the program of the Section of Chemical Education had been the most inspiring program that he had attended for a great many years from a teaching point of view. It seemed to be the unanimous opinion of those in attendance that the Section should be encouraged in every way possible. Chemists cannot be educated unless there are teachers of chemistry. Research work is of very great importance but the work of the conscientious, inspiring teacher is productive of a great deal more good from the chemical point of view.

J. C. OLSEN

BROOKLYN POLYTECHNIC INSTITUTE
BROOKLYN, N. Y.

The Lake Placid Meeting of the American Electrochemical Society

The Fall Meeting, September 29–October 1, was held at Lake Placid Club in the Adirondack Mountains of New York State. Nature brought out her finest colors to paint an unsurpassably lovely autumn landscape; the Society furnished an attendance of over a hundred members and friends; thirty investigators furnished a scientific program worthy of the best traditions of the Society.

With complete facilities for the technical sessions, the locality offered such attractions as the afternoon boat ride on Lake Placid, an afternoon climb up Mount McIntyre, a forty-mile auto ride through the mountains, and a golf tournament over a very "sporty" course.

Coming to the technical sessions, which occupied the three mornings, there were miscellaneous papers on Thursday, a symposium on "Nonferrous Electrometallurgy" on Friday, and a symposium on "Electrodeposition of Metals" on Saturday.

MISCELLANEOUS PAPERS

J. Newton Friend (London) proposes a "New Theory of the Corrosion of Iron." After noting some anomalies not explained by any of the current theories, he sets forth a new and more comprehensive theory based on considering the first product of corrosion to be *colloidal* ferrous hydroxide; this later oxidizes to ferric hydroxide hydrosol, which is then alternately reduced by contact with the iron and oxidized by contact with the air, thus catalytically accelerating the corrosion of the metal. When this sol flocculates or precipitates, it yields the ordinary rust. According to this theory, the oxidation of iron is at first a very slow process, but is rapidly accelerated by the catalytic activities of the colloidal oxidation products. Dr. Friend showed in a convincing manner how his new theory explained many difficult problems in iron rusting. It is possible that this paper opens up a new era in the study and understanding of this immensely important phenomenon.

Haakon Styri (Philadelphia) explained how ball-bearing spheres were protected from rusting during manufacture by slushing with oil. A prerequisite is a thorough preliminary cleaning by an oil emulsion in water, which leaves a thin film of oil. This protects also during grinding, and gives a fine finish. The paper gives results on nearly 1000 specimens, by a great variety of oils and greases.

C. J. Rodman (Pittsburgh) discussed the formation of oil sludge in transformers, giving descriptions and analyses of the different kinds, *i. e.*, asphaltic (due to oxidation), soapy (due to oxidation, absorption of moisture and action on the metal parts present), and carbonaceous (due to electrical breakdown). Careful selection of the oil and exclusion of air are recommended. Mr. Moody, in the discussion, pointed out that oil kept at 130° C. for 18 days with air excluded would become highly colored, and if air were admitted would also become sludged.

N. Kameyama (Tokyo) has determined the electrolytic dissociation of sodium and calcium cyanamides in water solution. That of the unhydrolyzed salts in solution is 81 to 91 per cent for the sodium salt and 72 to 86 per cent for the calcium salt, for dilutions of 10 to 80, respectively.

P. C. Alsgaard (Kristiania) described the electrolytic production of sodium perborate. Trygne Valeur continued the work of Kurt Arndt, and Alsgaard has continued that of Valeur. After many tests, an electrolyte was adopted containing (g. per liter): borax 45. Na_2CO_3 130, $NaHCO_3$ 45, $K_2Cr_2O_7$ 2, water glass 2. This was electrolyzed with a porous partition, and perborate was made at an ampere efficiency of 40 per cent. To produce 1 ton per day would require 450 h. p., 10 laborers, and about 7 kg. of platinum.

H. M. Goodwin and E. C. Walker (Massachusetts Institute of Technology) investigated the best conditions for electrolytic oxidation of hydrochloric acid to perchloric acid. They showed the effects of concentration of acid, current density, time, and temperature. A small cell is described in which 800 g. of 60 per cent acid can be produced per day. They suggest using two cells, the first run under the best conditions for producing chloric acid and the second under the best conditions for oxidizing chloric acid to perchloric.

Raymond Freas (New Orleans) discussed the general question of electrolysis of organic compounds, particularly the mechanism of the discharge of ions in electrolytes at platinum electrodes.

He divides the factors into the variable, nonvariable, and special. The action of colloids is said to be unexplained. A convenient experimental apparatus for such work is described.

A. Lowy and E. H. Haux (University of Pittsburgh) described the electrolytic oxidation of the leuco-base of malachite green. Their experiments showed the necessity of a catalyst, sulfuric acid as solvent, high temperature, and low concentration of the leuco-base in the anolyte. The highest dye yield was obtained with nichrome gauze anode, platinum cathode, uranyl sulfate as catalyst, and 85° C.

B. G. Worth (New York City) emphasized the importance of graphic control of electrolytic processes, in order to make visible to the eye the various factors which control these operations.

C. G. Fink and C. H. Eldridge (New York) described observations on electrolytic corrosion of lead-thallium alloys, noted when attempting to use them as unattachable anodes in copper sulfate plus sulfuric, nitric, and hydrochloric acid electrolytes. At Chiquicamata, Chile, duriron anodes corrode at the rate of 5 to 6 lbs. per 100 lbs. of copper deposited, lead anodes 65 lbs., while an alloy of Pb 70, Tl 10, Sn 20 was found in the laboratory to lose only 1.2 lbs. The low corrosion loss is ascribed to a very adherent film formed during electrolysis. The solution of tin and thallium in the electrolyte is, however, a disadvantage, and it was stated in the discussion that the problem of the unattachable anode in such solutions has been still further advanced by the use of an alloy containing 67 per cent of copper which is now in practical use, and does not introduce any impurity into the electrolyte which can be deposited with the cathode copper.

J. G. Thompson (Cornell University) investigated the electric furnace purification of zirkite, with the object of producing pure zirconium oxide for refractory purposes. The impure ore contains silica, which it was found could be 90 to 95 per cent eliminated by mixing with enough C to form SiC and heating above 2220° C., the decomposition point of the latter. Subsequent treatment of the residue with chlorine or phosgene is recommended for removal of iron.

M. L. Hartman and W. A. Koehler (of the Carborundum Company) tested the cross breaking strength of special refractory materials, produced in the electric furnace, compared with bauxite, magnesia, fire-clay, and silica bricks. In general, the recrystallized carborundum and bonded carborundum showed moduli of rupture ten to twenty times as great as the ordinary refractories. In the discussion, the practical usefulness of these special refractories for zinc retorts was noted.

F. A. Lidbury and F. A. Stamps (Niagara Falls) described a simple form of steam generator to be run by alternating current of 100 to 500 volts. The electrodes are concentric steel tubes, and ordinary water is used as the resistor and to generate steam. The discussion centered mostly around the special economic conditions which made it profitable to raise steam electrically, such as those in Scandinavia during the war, where buildings with steam heating plant could be provided with electric steam generators, when coal was costing $50 to $100 per ton, and thus the cost of electric heating appliances saved. Also industrial plants needed steam for some operations, which could be furnished cheaper electrically than by burning fuel. It was also pointed out that there is a dearth of data concerning the conductivities of electrolytes above 100° C., and the action of steam on insulators at these moderately high temperatures.

H. M. Goodwin and L. A. Wilson (Massachusetts Institute of Technology) detailed experiments on the effect of pressure on overvoltage. They used copper, nickel, and mercury cathodes, and varied the pressure from 760 to 20 mm. Hg. In all cases the overvoltage was constant for pressures around 40 mm. and over, but increased rapidly for lower pressures, on an equilateral hyperbole curve. This agrees with MacInnes and Adler's theoretical treatment of the phenomenon.

SYMPOSIUM ON NONFERROUS ELECTROMETALLURGY

W. A. Cowan, L. D. Simpkins and G. O. Hiers (National Lead Co.) described Frary metal, and electrolytically produced Ca-Ba-Pb alloy used as bearing metal. A low-melting point mixture of calcium and barium chlorides is electrolyzed over molten lead as cathode, until some 2 per cent of calcium and barium is in the lead. This addition makes remarkable changes in the physical properties of the lead, particularly in its hardness, which runs up to 30 Brinell. The hardness increases noticeably some 10 to 20 per cent, on aging for a month; heat treatment also increases the hardness, in some cases doubling it. (The exact heat treatment is not described.) The alloys are used for bearings, die castings, extruded rod and pipe. A particular characteristic is that while Frary metal is of approximately the same hardness as ordinary good Babbitt metal at ordinary temperatures, it loses much less hardness when running at 100° to 150° C. In the discussion it was pointed out that the ampere efficiency of production of the alloy is below 20 per cent, leaving a large margin for the electrolytic expert to improve it.

Chas. Vickers (Buffalo, N. Y.) described the use of sodium, silicon, calcium, barium, and strontium, and combinations of the same, as deoxidizing agents for copper, brass and bronze. He concludes that sodium-copper or sodium-tin is a better deoxidizer for bronze than phosphor-copper, giving a tougher bronze; calcium-copper alone (10–15 per cent Ca) is not dependable to produce sound copper castings, calcium-silicon-copper (7–10 per cent Ca, 3–5 per cent Si) is better, but the addition of another alkaline-earth metal to this combination gives best results. On account of patent matters the last element was not named; it was stated that this triple deoxidizer was also excellent for monel metal and other high-nickel alloys. Barium-tin (10 per cent Ba) was made by electrolysis and used on brass and bronze, but the results are not yet completely investigated.

E. A. Smith (Birmingham, England) described modern developments in the British brass industry. Details were the development of works laboratories, coöperative research, syndication of the industry, foundry practice, extrusion, hot pressing, forging, rolling, annealing, etc. He states that the high cost of power has delayed the introduction of electric melting furnaces, but this excuse is only partly true. The majority of British brass works are described as very small, and unable to use the large electric furnaces. Certain it is that Great Britain lags far behind the United States in this development.

H. M. St. John (Detroit) discussed the influence of the electric furnace on the metallurgy of nonferrous metals. He regards the standardized electric melting furnace of to-day mainly as a machine, which can be put into the hands of a mechanic who has only to follow instructions. The man who issues the instructions should have metallurgical skill and experience, but the operator need have neither. Electric melting is dissipating the traditional secretiveness of the nonferrous industries; it has revolutionized metal-handling methods, and produces a more uniformly high quality of product, with less labor and waste of metal. Compared with open-flame and reverberatory furnaces, the average over-all costs are two-thirds; compared with crucible melting, one-half. The discussion took up the contracts for power to run such furnaces, and their power factor. The author stated that an electric melting furnace load usually had a power factor of 85 per cent or over, and that it really improved the average power factor of the average power station.

N. K. B. Patch (Buffalo) made comparisons of electric furnace practice with fuel-fired furnace practice. His experience was that the results were practically alike in regard to costs, but that the electric furnace is cleaner and more comfortable to operate, and some sensitive alloys are of better quality when melted electrically.

T. F. Baily (Baily Electric Furnace Co.) described his resistance type of electric furnace for melting brass and other nonferrous metals. He claims that this type, since it can be tightly closed, makes metal of better quality; also that it is simpler in construction and operation than any other; he admits that it takes more current to melt a charge, but gives a better electrical load factor; has a more accessible hearth, and is more easily repaired. Some of these claims were disputed in the discussion.

H. A. Winne (General Electric Co.) described recent developments in electric furnaces of the muffled arc type, for melting 1500 to 2250 lbs. of brass per hr. Heat is generated by current flowing through contact arcs and by muffled arcs in broken graphite. This gives a heat source of large area and comparatively low, uniform temperature. Heat is conducted through carborundum bridge walls to the metal in contact with them; it is also radiated down from the roof. Run continuously, the 1500-lb. furnace melts one heat per hour, using 300 kw. hr. per ton—a net efficiency of about 50 per cent. These furnaces can melt charges up to 1500° C. (2730° F.); they are particularly suitable for melting alloys containing volatile ingredients, because of the low temperature of the resistors.

H. A. DeFries (New York City) described melting of silver in electric furnaces. He says it eliminates high crucible costs and the necessity of great experience for the melter. Pure bar silver should be gradually heated up to 1205° C. and poured at 1093° C. Pure silver or sterling alloy intended for rolling mill stock or castings, however, should be cast at 1293° to 1304° C., when cast into nearly horizontal molds, and at 1204° C. when cast into vertical molds. A block of iron put into the bath absorbs the oxygen and keeps the metal from spitting. The travel of metal from furnace spout to mold should be as short as possible. Molds should be smoked and warmed up to about 204° C. (400° F.). In a furnace holding 10,000 oz. (790 lbs.) 6.6 lbs. were melted per kw. hr. In the discussion, Dr. Northrup stated that he had melted 10.6 lbs. of silver per kw. hr. in his oscillating-current induction furnace. These figures show thermally 38 and 60 per cent melting efficiency, respectively.

F. C. Thompson (Sheffield University, England) discussed the advantages of the electric furnace melting of nickel silver. Arc furnaces, he says, should not be used because of large volatilization of zinc around the electrodes. Experiments with a small Kjellin induction furnace did not give good results. The resistance furnace appears the only type suitable for this particular alloy. Losses of zinc are less than in crucible melting. Less gases are occluded by the metal, and no carbon is absorbed.

Robert J. Anderson (Bureau of Mines, Pittsburgh) described the various alloys of aluminium and copper, in a 30-page paper. The information was well collated, timely, and complete.

W. R. Ingalls (New York City) discussed the electrometallurgy of zinc. In the line of electrolytic extraction nothing new was given, but in the line of electric furnace smelting very interesting details were given of the processes used at Trollhättan, Sweden. There roasted zinc ores containing lead, copper, and silver are reduced in large electric furnaces, producing lead-zinc blue powder in the attached condensers, but no reguline metal. This powder is then rubbed in the Cornelius rotating electric furnace, which brings the larger part of it out in the form of a zinc-lead alloy. The residue is returned to the ore furnaces. The alloy is distilled, yielding high quality zinc and pure lead. The electrolytic zinc is purer than electrothermal zinc, and therefore commands the preference for making fine brass. The electrolytic process is cheapest on the poorer ores; the electrothermal process should only be used on the richer ores. Mr. Hale, in the discussion, pointed out the great advantage of the electrothermal process in saving lead, copper, and silver which were in the ore, which required extra expense to save in the electrolytic process.

SYMPOSIUM ON THE ELECTRODEPOSITION OF METALS

The rest of the papers were specifically devoted to a symposium on the electrodeposition of metals, under the auspices of the newly formed "Electrodeposition Division" of the Society, presided over by Dr. Wm. Blum, of the Bureau of Standards, Washington.

C. J. Wernlund (Roessler & Hasslacher Chemical Co.) set forth his studies on the zinc cyanide plating solution. He detailed a long series of experiments using 1.5 to 6 per cent solution of zinc cyanide, to which varying amounts of sodium cyanide, caustic soda, and sodium carbonate were added, with and without organic addition agents. The best solution of all those tried contained 6 per cent $Zn(CN)_2$, 5.25 per cent NaCN, 0.75 to 1.5 per cent NaOH, 3 per cent Na_2CO_3, 0.75 per cent NaF, 0.75 per cent corn sugar, 0.11 per cent gum arabic, and was worked at 40° to 50° C. The maintenance of the solution is primarily a question of keeping a small amount of free NaCN always present. Current efficiencies are 50 to 75 per cent at the cathode and 90 to 110 per cent at the anode. The best test of good plating is the salt-spray test, to determine the actual protective power of the coating; using this test, the zinc cyanide deposit gives a better rust-proof coating than the zinc sulfate bath.

W. A. Hughes (London) described researches on the electrodeposition of iron. Almost all the processes described in the literature had been tried by the author, and he detailed his experiences with them in a 40-page paper. He found Maximowitch's method the most generally useful. In the discussion it was noted that the recent commercial work in France had been omitted from the paper, and also a promising method of recovering both iron and sulfur from pyrrhotite ore devised by Mr. Eustis, of Boston, in which the ore was leached with ferric chloride solution to dissolve the iron, the latter deposited out electrolytically, regenerating ferric chloride solution, which was then returned to the leaching vats, while sulfur and the gangue of the ore only remained in the latter. It was the general opinion that many details would have to be worked out before such a cyclic process became commercial.

W. Blum and H. E. Haring (Bureau of Standards) described the electrodeposition of lead-tin alloys. With a certain ratio of lead to tin in solution, an alloy or mixture of nearly equal parts can be plated out. The proportion of each depends only on their ratio in the solution, and is at any moment independent of the kind of anode used. The use of an addition agent had the same effect as increasing the current density. The process is used by our Navy Department for coating the inside of airflasks of naval torpedoes. It may have other commercial applications.

W. Blum (Bureau of Standards) discussed the structure and properties of alternately electrodeposited metals, basing his paper on experience at the U. S. Bureau of Engraving, in alternating thin copper and nickel deposits, in order to stiffen and improve the copper for engraving purposes. When layers of nickel about 0.004 mm. thick were alternated with layers of copper 0.02 thick, the composite plate was much stronger and finer grained than a thick copper plate. The thin deposits seemed to inhibit development of large and irregular crystals, thus giving the fine-grained effect, while the alternation probably caused the greatly increased mechanical strength. The principle may be applicable to many other metals and for many other purposes; the author even speculated as to what might result if the alternate layers were so thin as to have molecular dimensions. In the discussion it was stated that the crystalline nature of the primary cathode surface might influence that of the deposited metals, even through several alternate deposits. It was agreed that the whole subject was of great theoretical as well as practical interest.

J. W. RICHARDS

LEHIGH UNIVERSITY
SOUTH BETHLEHEM, PA.
October 4, 1921

A. C. S. Section Meetings, 1921-1922

CHEMICAL SOCIETIES IN NEW YORK CITY, RUMFORD HALL, THE CHEMISTS' CLUB

October 7—American Chemical Society.
October 14—Société de Chimie Industrielle.
October 21—Society of Chemical Industry. *Grasselli Medal Award.*
November 11—American Chemical Society. *Joint Meeting* with Society of Chemical Industry, American Electrochemical Society, and Société de Chimie Industrielle.
November 18—American Electrochemical Society.
December 2—Society of Chemical Industry.
December 9—American Chemical Society.
January 6—American Chemical Society.
January 13—Society of Chemical Industry. *Perkin Medal Award.*
February 10—American Electrochemical Society. *Joint Meeting* with Society of Chemical Industry, Société de Chimie Industrielle, and American Chemical Society.
March 10—American Chemical Society. *Nichols Medal Award.*
March 24—Society of Chemical Industry.
April 21—Society of Chemical Industry. *Joint Meeting* with American Electrochemical Society, Société de Chimie Industrielle, and American Chemical Society.
May 5—American Chemical Society.
May 12—Société de Chimie Industrielle. *Joint Meeting* with American Chemical Society, Society of Chemical Industry, and American Electrochemical Society.
May 19—Society of Chemical Industry.
June 9—American Chemical Society.

ROCHESTER SECTION

Meetings of the Rochester, N. Y., Section of the SOCIETY will be held as follows:

October 17
November 7 and 21
December 6 and 19
January 9 and 23
February 6 and —
March 6 and 20
April 3 and 17
May 1 and 15

Calendar of Meetings

American Institute of Chemical Engineers—Annual Winter Meeting, Baltimore, Md., December 6 to 9, 1921.

American Association for the Advancement of Science—Annual Meeting, Toronto, Canada, December 27 to 31, 1921.

American Ceramic Society—21st Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922.

NOTES AND CORRESPONDENCE

Liability for Laboratory Explosions

In 1916 Miss Louise Hamburger of Brooklyn, a first year student in Cornell University, lost an eye as the result of an explosion in a glass test tube in which she was heating a mixture. Suit was brought against Cornell University, and on October 4, 1921, after a trial by Supreme Court jury in Binghamton, N. Y., Miss Hamburger was awarded $25,000 damages. It is understood that the case will be appealed to the highest courts. The far-reaching effect of such a decision, if it is upheld by the highest Court, is so great that we have asked Professor L. M. Dennis, head of the Department of Chemistry, Cornell University, for an outline of the case as it was presented by both sides to the Court. In response to our request, Professor Dennis has furnished the following statement:

On the afternoon of January 12, 1916, a section of the class in Introductory Inorganic Chemistry was instructed to perform several experiments described in the "Laboratory Manual of Elementary Chemistry" by Dennis and Clarke. The first of these experiments, No. 84, is stated in the Manual as follows:

> Pulverize 1 g. of potassium chlorate in a mortar, add to it 9 g. of strontium nitrate, and thoroughly mix the two substances. Empty out the contents of the mortar on a piece of paper, wash the mortar thoroughly, wipe it dry, and grind in it 3 g. of shellac. Add this to the substances on the paper, and carefully mix them with as little friction as possible. (Do not grind the shellac in the mortar with the other ingredients. An explosion would result.) Place the mixture on a brick or tile and ignite.
>
> If properly prepared, it should burn with a brilliant red flame.

The bottles of "Commercial" potassium chlorate were set out on the side-tables in the laboratory for this experiment, "Commercial" potassium chlorate being furnished instead of pure potassium chlorate, because it would answer the purposes of the experiment just as well as the pure substance, and, further, because of its low cost as compared with pure potassium chlorate.

A later experiment that was to be performed that afternoon, Expt. 88, is stated in the Manual as follows:

> Mix 2 g. of mercuric sulfide with an equal weight of powdered lime and heat the mixture in a hard-glass tube until the residue assumes a dark yellow color.
>
> What collects in the upper part of the tube?
>
> What is left in the lower part?
>
> Shake out this residue and add to it dilute hydrochloric acid. Note the odor of the escaping gas.
>
> What is it?

In this Introductory Course, the commoner chemicals needed during that afternoon were placed in tall glass bottles on side-tables in the laboratory. Mercuric sulfide, being needed only for this one experiment in the course and being a somewhat expensive chemical, was given out from the stockroom adjacent to the laboratory. Before the class came into the laboratory, one of the assistant instructors on our staff went into the stockroom, emptied out on a large sheet of Manila paper a quantity of black mercuric sulfide from the stock-bottle in the room, and instructed the attendant in the stockroom to place upon small squares of Manila paper about 2 g. of the substance, so that these small portions could rapidly be handed out to the students when they came to the stockroom window for it. The instructor showed the stockroom attendant about how much of the substance to take up on a spatula and place on each of the small papers. The class assembled for their laboratory work, and one young woman in the class, after receiving instructions in the laboratory as to how the experiment was to be performed, came to the stockroom window and received about 2 g. of mercuric sulfide on one of these papers. This she took to her desk in the laboratory, and the assistant instructor in charge of the small group to which she belonged told her to go to one of the side-tables and obtain from the proper bottle there the powdered lime. He then passed on to the other students of his section. The young woman returned to her desk with the material that she had taken from a bottle on the side-table, placed this material in a porcelain mortar with the mercuric sulfide that she had obtained from the stockroom, and mixed the two substances in the porcelain mortar. She then asked the instructor who was standing near her how the hard-glass tube should be closed at one end, and since she was behind in her work, he sealed this tube for her and gave it to her. He then watched her place some of the mixture from the mortar in the tube, and when about one inch of the powder had been added, he told her that that was enough for the experiment, and that she need not use the rest of the mixture in the mortar. He then passed on to other students and heard an explosion at the other end of the laboratory where a group of students in charge of another assistant instructor were working. A few moments afterward he heard a loud report near him and turned to see that an explosion had occurred in the experiment that the young woman in question was performing and that she had been injured. The time that elapsed between the two explosions was from one to two minutes.

A member of the staff promptly gave first aid to both the students who had been injured by the explosions in the experiment and they were hurried to oculists in the city. The stockroom attendant was ordered by one of the assistant instructors to give out no more mercuric sulfide until he received further word from the instructor in charge of the laboratory. The instructor in charge requested his assistants to go out into the laboratory immediately and collect from the three side-tables all the bottles of lime, potassium chlorate, and strontium nitrate that were standing on the side-tables; these three being the only white chemicals set out that day for the experiments of this section. The mortar on the young woman's table, which contained the unused remainder of the mixture that she had prepared for this experiment, and the unused remainder of the mixture from the table of the other student were immediately brought in to this instructor, together with some of the mercuric sulfide from the stockroom. He made an examination of the materials in the bottles from the side-tables in the laboratory with the aid of a direct-vision spectroscope and found that, except for the weak sodium line that is always seen when the spectrum of a substance that has been exposed to the air is examined, and which, as all chemists know, is caused by the presence of very minute amounts of sodium compounds such as common salt in the atmosphere, the bottles marked lime showed the presence of calcium but no other metal; the bottles marked potassium chlorate showed the presence of potassium but no other metal; and the bottles marked strontium nitrate showed the presence of strontium but no other metal. He made chemical examination of the mercuric sulfide that still remained in the bottle in the stockroom and from which the supply for the students had been taken and found that the substance contained mercury and sulfur. He also examined this mercuric sulfide with a spectroscope to ascertain whether it contained compounds of potassium or calcium or strontium and he found that the substance yielded none of the spectrum lines of these three elements. He did, however, see in the flame spectrum of the mercuric sulfide, flashes of the sodium line.

The residual substance in the mortar that the young woman had used was handed to Professor Chamot of our staff, a leading expert on chemical microscopy, and was carefully examined by him under the microscope. He promptly reported to Dr. Dennis that it contained potassium chlorate and mercuric sulfide and that it contained no lime. He obtained the same results upon examination of the mixture used by the student who had the first explosion.

The evidence above cited, brought forward by the Department of Chemistry, appeared to show beyond question that the young woman obtained the proper chemical, mercuric sulfide, at the stockroom window, but that when she went to the side-table to obtain the powdered lime, she took potassium chlorate from another bottle and mixed that with the mercuric sulfide instead of using the powdered lime as directed. The defendant claimed that the explosion was due to this mistake on the part of the student, and that it resulted from the heating together of mercuric sulfide and potassium chlorate, contrary to the instructions given under Expt. 88 in the "Laboratory Manual."

The plaintiff testified that she went to one of the side-tables in the laboratory to get the powdered lime for the experiment and found that this bottle was being used by another student in her section. She stated that she waited until he was through with the bottle and that she then took up the bottle, looked at the label, which she testified was "CaO," and measured out the proper amount of that white substance. It was shown during the trial that the student who, according to the plaintiff's testimony, took some of the material from the bottle marked "lime" just before she did, conducted Expt. 88 successfully and without explosion. The plaintiff offered no evidence as to what chemical the student who had had the first explosion had mixed with the mercuric sulfide, or as to the source from which he obtained this second chemical. Her evidence did show, however, that he did not get it from the same bottle on the side-table that she had used. The two explosions above noted were the only ones that occurred during that afternoon, and the student who had had the first explosion in the performance of Expt. 88 stated soon afterward that his accident was entirely due to his own carelessness in that he picked up a white chemical that had been spilled on one of the side-tables instead of taking some lime from the bottle labeled "lime." The Court excluded this statement on the ground that it was hearsay. At least fifty of the students in the laboratory on the afternoon in question performed Expt. 88 with successful results and without mishap. It was also brought out that Expt. 88 had been performed during the preceding ten years by about 10,000 students with successful results and without accidents or explosions occurring in any case.

A witness for the plaintiff, retained as an expert, testified that in his opinion the explosion must have resulted from some cause other than the heating of a mixture of potassium chlorate and mercuric sulfide, because he had made many experiments upon this point and no explosion had in any case resulted when these two substances were heated together in a hard-glass tube sealed at one end. The defendant, on the other hand, brought forward testimony to show that experiments conducted since the beginning of the trial demonstrated that a mixture of equal weights of mercuric sulfide and potassium chlorate would at times explode with great violence when heated under the above conditions, and that if a minute trace of dust or paper fiber were present, a violent explosion occurred in about half of the trials. The plaintiff argued that if dust or other organic matter would increase the possibility of explosion in this experiment, the Department of Chemistry was negligent in that it furnished the students with "Commercial" potassium chlorate for the experiments in the Manual instead of giving them "Chemically Pure" potassium chlorate, since the "Commercial" potassium chlorate might contain small amounts of paper fiber or other organic substance. To this the defendant replied that there was no experiment in the course that called for the heating together of mercuric sulfide and potassium chlorate and that in the two experiments in the Laboratory Manual in which "Commercial" potassium chlorate was used, the presence of a slight amount of organic matter in the potassium chlorate would not have caused accident to the student if these two experiments were performed according to the instructions given in the Manual. When asked why "Commercial" potassium chlorate was furnished to the students for any experiment instead of "Chemically Pure" potassium chlorate, a witness for the defense stated that, since the students in the laboratory courses are required to pay for the chemicals that they use, it was the manifest duty of the Department toward the student to furnish the cheaper "Commercial" potassium chlorate rather than the much more expensive "Chemically Pure" substance, if the cheaper chemical could be used in the experiments for which it was intended just as safely and as satisfactorily as the more expensive grade.

The plaintiff further argued that if the spectroscopic examination of the material showed the yellow line due to sodium, the sodium was probably present as metallic sodium in the mercuric sulfide, that the presence of this metallic sodium probably caused the explosion, and the Department of Chemistry was negligent in that it did not furnish the students with mercuric sulfide free from metallic sodium. To this the defendant replied that the sodium line in the spectrum does not indicate that metallic sodium as such is necessarily in the substance under examination, and that in the case of the chemicals in question, it would be quite impossible for metallic sodium to be mixed with the finely powdered chemical in the process of manufacture and remain as metallic sodium during long contact with the air; that the sodium line seen in the spectrum of the mercuric sulfide was undoubtedly due to the presence of a compound of sodium, such as sodium hydroxide or sodium chloride, that such substance was probably present only in minute amount, and that either of the two above compounds of sodium, even if present in large amounts in the mercuric sulfide, could not have caused an explosion when the mercuric sulfide was heated with powdered lime.

Regarding the purchase, storage, and handling of chemicals in this laboratory, the defendant testified that all chemicals were purchased from accredited firms, and were received, unpacked, stored, and arranged in the storerooms in the basement by a man who, although not trained as a chemist, had had forty years of experience in the service of the department in this kind of work; that chemicals needed in the upper stockrooms were either taken up to those stockrooms from the storeroom in the original containers or were transferred by a member of the staff of instruction from the large containers in the storeroom to smaller containers labeled to correspond with the original package; and further that the duties of the stockroom attendants were confined to handing out to students, on the students' written orders, apparatus and chemicals, and that these men did not prepare any mixtures of chemicals or any solutions of chemicals.

Upon the day of the accident, when the small amounts of about two grams each of mercuric sulfide on slips of paper were given to the students in Introductory Chemistry, an office boy in the employ of the Department was in that particular stockroom engaged in one of his regular duties, namely, the sorting and placing in pigeonholes of the order-slips of the students. To speed up the delivery at the stockroom window of the mercuric sulfide to the students on that day, this boy was asked by his father, who was in charge of that particular stockroom, to stand at the window and slide forward to the students these squares of paper carrying two-gram samples of mercuric sulfide. The plaintiff claimed that the Department was negligent in allowing a young boy about fifteen years of age to dispense chemicals to the students. It was shown that all that he did on the day in question was to render service as above stated.

Upon cross-examination, counsel for the plaintiff asked witnesses for the defense whether the chemicals as received from the manufacturers were analyzed or otherwise tested to ascertain whether each chemical in its container corresponded exactly with the label on the container. The defense replied that it did not so test the chemicals, but that it assumed that the chemicals were correctly labeled by the manufacturer. The plaintiff further asked whether when a bottle in a stockroom or the bottles on the side-tables in the laboratory are filled from the original containers in the basement storeroom, the contents of each bottle thus filled is examined or analyzed by the Department to ascertain whether the label on the container still exactly accorded with the contents of the bottle. The Department replied that it does not test the contents of each container thus filled, but that on the contrary, the filling being done by a member of the staff of instruction, it holds that such transfers are accurately made by trained chemists and that it is unnecessary to test the contents of each of these small containers before allowing the students to any of the chemicals. The plaintiff argued that this evidence showed that the Department was negligent in that it did not always analyze or examine the contents of each and every container in the laboratory before the students were allowed to use any of these chemicals in their experiments.

A very important feature of the case was the ruling of the Court that it was the duty of the Department of Chemistry to analyze all chemicals received from manufacturers, for the purpose of ascertaining whether the contents of the container agreed exactly with the label on the container before any of these chemicals were dispensed to students. The Court further ruled that it was the duty of the Department to ascertain by chemical examination whether the contents of all bottles in the student laboratories that had been filled from the original containers were in exact accord with their labels.

The theory of the plaintiff was that the young woman was given a wrong chemical from the stockroom or that the bottle marked "lime" on the side-table in the laboratory contained some chemical other than lime that caused the explosion. The defendant refuted this theory by showing through the testimony of Professor Chamot that the bottle marked "lime" on the side-table in the laboratory that the young woman should have used contained lime and nothing else, and that the bottle marked "potassium chlorate" on that side-table contained potassium chlorate and nothing else; and that the unused remainder of the mixture that the young woman had prepared for this experiment contained mercuric sulfide and potassium chlorate, but no lime. The defendant further showed that many other students in that laboratory section on that afternoon had performed the experiment according to the directions that had been given to them and had obtained the usual results. The evidence brought forward by the defendant demonstrated that no mistake had been made in the issuance of chemicals to the students that afternoon, and that the contents of the several bottles on the side-tables in the laboratory corresponded to the labels on the bottles, and the defendant argued that this evidence showed conclusively that the two explosions that occurred in the performance of Experiment 88 must have been due to the carelessness of the two students concerned, who undoubtedly mixed with the mercuric sulfide, not lime as had been directed, but potassium chlorate.

A Fire Blanket Receptacle

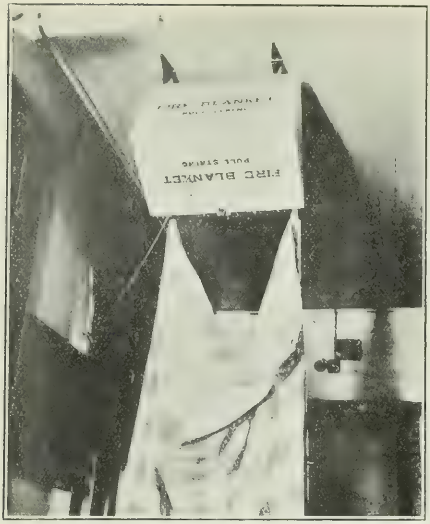
Editor of the Journal of Industrial and Engineering Chemistry:

In these days of "Safety First" it is fitting that chemists, who know the properties of materials, including their hazards, should guard against the attitude of mind expressed by the adage "Familiarity breeds contempt." On the contrary they should put themselves in the van of that army which seeks to lessen the menace to life, health, and property, for themselves, their fellow employees, and their employers.

Every man, woman or child has known occasions when a woolen blanket, promptly and properly used, would have smothered flames and saved a human life. Fire blankets are necessary equipment and commonly used in laboratories, but a suitable place to keep them is much less common. A fire blanket is usually kept in a drawer, but drawers are not always centrally located or in the place of easiest access, they sometimes stick, and there is always the chance of a blanket in a drawer being covered with other articles. Also drawers are not dust-free, and mice are apt to build nests in them or to cut the blanket.

These considerations led to the design of the following device, which eliminates all of the disadvantages mentioned, keeps the blanket where it is always out of the way, and in addition produces the blanket unfolded and in a position for instant use in about one second. "Time is the essence" of this matter, for a few seconds might mark the difference between life and death, or the loss or the saving of a building.

This blanket holder consists of a triangular box, hinged to the ceiling and held closed by a spring catch, which when released by jerking a cord, allows the box to fall open and swing back, and the blanket to drop out, unroll and hang ready for one with burning garments to wrap himself. The blanket has a canvas loop sewed to each corner of one end, and these loops are suspended from screw hooks in the ceiling by means of a twine



string, doubled, and of such length as to bring the lower end of the blanket almost to the floor. If one wishes to smother a fire on a table or to carry the blanket to another person in distress, it is easy to jerk the blanket down, breaking the strings. The screw hooks are placed so that when the box is closed, they are within the box, near the front, and about an inch from the ends. A ring of about 1 in. diameter is tied to the end of the releasing cord.

The box is about 22.5 in. long, and is shaped like a trough, the two sides being 15 in. wide and placed at right angles to each other. The ceiling serves to close the third side. Blocks 2 in. thick separate the hinges from the box to cause the latter to swing back farther.

The blanket is rolled so that the canvas loops come at the two ends of the roll. First spread the blanket flat upon the floor. Then fold the two sides over, bringing the two edges each to the opposite side, the blanket now being folded to three thicknesses. Then turn the edges of the two top thicknesses back to the outside again. This is shown by the bent line, $\underline{><}$ which represents either end of the blanket. In rolling the blanket, one should begin at the end without the loops.

L. S Bushnell

Freeport Sulfur Company
Freeport, Texas
May 30, 1921

Nitrocellulose and Its Solutions as Applied to the Manufacture of Artificial Leather—Correction

In the article by W. K. Tucker under the above title [This Journal, **13** (1921), 623] the number 1.965 in line 12 of the second paragraph should read 1.065.

WASHINGTON LETTER

By Watson Davis, 1418 Rhode Island Ave., N. W., Washington, D. C.

Proposed Alcohol Legislation

While Washington is preparing for the disarmament conference, at which chemical warfare is sure to be discussed, Congress has before it a proposal that if adopted is likely to disarm the beneficial and legitimate chemical and pharmaceutical industries by making the legitimate use of ethyl alcohol still more difficult and expensive than it is now.

The Senate Finance Committee majority has agreed to an extra tax of $4.20 per proof gallon on grain alcohol, with the provision that this sum shall be rebated on proof of the medical or otherwise legitimate use of the alcohol. This is in addition to the present tax of $2.20 per proof gallon. This provision, which was supported by the agricultural "bloc" in the Senate, in the House originally called for a straight nonreturnable tax to be paid by the person responsible for the diversion of the spirits to beverage purposes.

A serious setback to the chemical and drug industry of the country that relies on alcohol to a fundamental extent is foreseen if this provision, intended to strengthen the prohibition act, is made a law. It is estimated that 170 to 200 millions of dollars will be continuously tied up in the U. S. Treasury for at least three months. Based on present consumption, this is the amount of extra tax that would have to be paid and it is conservatively believed that this is the minimum of time that would be required for the rebating. While this would vitally affect every chemical industry of the country as well as every chemist, manufacturers and dispensers of pharmaceuticals would be particularly affected. As an example, Parke, Davis and Co., of Detroit, one of the largest of the manufacturing druggists, would have to keep approximately $1,500,000, all non-interest bearing, in the national treasury continuously. This amount is approximately three-fourths of their capital. The 50,000 retail druggists of the country would, on a basis of using 10 wine gallons of ethyl alcohol a month, pay $3,999,000 a month, or have nearly $12,000,000 unprofitably invested in Uncle Sam's treasury if the refunding took only three months.

Because ethyl alcohol is 190 proof, the tax on a wine gallon, the gallon used in trade, would total $12.16 instead of $4.18 as now. Grain alcohol, which can be manufactured for about thirty cents a gallon, would sell for about $13.00.

How the rebating of the tax could be accomplished is bothering those interested in chemicals and drugs. The extra tax would have to be paid by the distiller or the proprietor of the bonded warehouse on withdrawal from bond. He would be forced to pass the tax on to the wholesaler, who would collect from the retailer, who in turn would be forced to add the excess tax to the price of the drugs in which the alcohol is used, and the public would pay. When the rebate is finally made, to whom should it go? That is the question that is bothering the interested parties. The druggists and chemists look forward with misgivings to the task of accounting for the legitimate use of every cubic centimeter of grain alcohol that they buy, which might even require the listing of each of the many times that they use alcohol in making a reagent or filling a prescription.

Opposition to this alcohol tax is attempting to impress itself on the senators. Among those who have protested are the American Drug Manufacturers Association, the American Pharmaceutical Manufacturers' Association, the National Wholesale Druggists' Association, the National Association of Retail Druggists, the Manufacturing Perfumers' Association, the Proprietary Association, the Flavoring Extracts Manufacturers' Association, the National Confectioners' Association, the Industrial Alcohol Manufacturers, and the American Pharmaceutical Association.

These organizations claim that the payment of the excess tax, which is in effect a fine, would make law-abiding citizens criminals in the eyes of the Government until they have proved themselves innocent. They consider that the excess tax would not promote the use of alcohol "in scientific research and in the development of fuel, dye, and other lawful industries" as the prohibition act provided, but would greatly hinder it and in some cases kill it altogether.

Chemical Warfare and Disarmament

The question of chemical warfare and disarmament is sure to play a large part in the coming conference in Washington. While little has crystallized, officially or unofficially, the probabilities of the situation can be summed up.

It is likely that the various countries will stand pat when it comes to the prohibition or limitation of the use of gas and other chemical means in warfare. Even before the war the United

States did not become a party to the Hague treaty prohibiting the use of gas in war, although Germany signed it and was afterwards the first to use gas in battle. It would be logical if American delegates should again refuse to become a party to gas warfare limitations. France is likely to oppose disarmament of any sort unless her safety from Germany is guaranteed by the other powers.

Chemical warfare has come to stay, in the belief of many who point out that no huge coast defense guns or floating fortresses that cost fortunes to build and maintain are necessary in battles fought with gas. It is only a twist of the wrist from poison gas and explosives to dyes, medicines, photographic chemicals, and a hundred other chemical necessities. A slight change in the making of indigo and you have mustard gas. General Fries, Chief of the Chemical Warfare Service, tells how the Polish army in its recent campaign needed hydrocyanic acid gas, and how they got it from Germany. Under terms of the treaty of peace Germany could not send them the gas as gas, but there could be sent the sodium cyanide and sulfuric acid which when combined give off the deadly gas.

To limit chemical armament it would be necessary to stifle the chemical industries. This would not only be dangerous for the peace-time welfare of the country, but the group of nations that limited chemical armament would be at the mercy of the countries that developed their chemical industries into powerful potential war factories. Chemical warfare preparation is inexpensive in time of peace, and reduction in cost of armament is understood to be one of the objects of the conference that opens November 11.

CONGRESSIONAL ACTIVITIES

News of the railroad strike called for October 30 is the topic of conversation in Washington to-day, and this matter is expected to occupy Congress during the week.

The Senate has been concentrating on the tax bill, and hardly a thought has been given to the tariff bill, although it is now planned to hold hearings on the agricultural schedules beginning about November 1. The dye embargo has laid dormant with the rest of the bill, and it is impossible to say what effect the action taken at the meeting of the American Chemical Society in New York has had on the senators. A group of experts of the Tariff Commission are collecting information for the use of the Senate Finance Committee on the effect of the American valuation basis for assessing customs duties.

The emergency tariff, together with the dye licensing provisions, will be extended until February 1 under a bill favorably reported by the House Ways and Means Committee. It is expected that this measure will become a law promptly although there may be a small amount of opposition in the Senate.

Hearings on the metric bill, that would introduce the metric system of weights and measures in this country, have been held during the past week. So far only the proponents of the bill have been heard, but these have included scientists and manufacturers. During the next week it is expected that Secretary Parsons will tell the Senate Committee on Manufactures, holding the hearings, that the American Chemical Society is in favor of the bill.

THE UNEMPLOYMENT CONFERENCE

The unemployment conference, which was headed by Secretary of Commerce Hoover, has closed its sessions after mapping out a constructive program on which representatives of capital and labor both agreed. By arousing governors of states, mayors of cities, and community authorities generally to the need of handling their own unemployment problems, this conference, which was called by the President, felt that a great step has been taken toward meeting the emergency situation. While the Federal Government can assist in providing employment, it has been brought out very clearly that the only wholesome way to deal with the problem is on a decentralized basis. Specific recommendations have been made by the conference covering unemployment in various industries. Many recommendations bear upon permanent measures looking to the prevention of unemployment in the future.

The question of the future of Muscle Shoals is still undecided. The army engineers and the engineering representatives of Mr. Ford are now trying to arrive at the cost of the completion of the dams that must be finished, and when this question is settled it is probable that further progress will be made.

Gas and phosphorus bombs were used in the recent airplane attacks on the old battleship Alabama, and officers of the Chemical Warfare Service are gratified over the results. Tear gas penetrated the ship and for four hours prevented the boarding of the ship without masks. Phosphorus was sprayed over the whole ship by the bomb dropping.

A general conference of petroleum men will probably be held in Washington in December. This conference is now being discussed by government officials and those interested in oil work here. Present indications are that the plans will be completed during November.

The dye section of the Tariff Commission, headed by C. R. DeLong, has been gathering statistics on the lithopone industry for the first six months of this year, and expects to have a report ready shortly.

The expert who will have charge of the chemical division in the Bureau of Foreign and Domestic Commerce of the Department of Commerce has not been appointed yet, nor has the head of the paper division been selected. Carl H. Greene of New York has been placed in charge of the specialties division.

October 16, 1921

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

THE OPPAU CATASTROPHE

The Oppau catastrophe has brought to a close the discussions on the relative value of the Claude and Haber processes. I have already discussed this subject with you often, but this accident, deplorable from the point of view of the human lives which it has cost, has resulted indirectly in certain conclusions.

The report of the investigating commission, although kept secret, points to these conclusions, according to the reports which I have been able to gather: (1) From the point of view of ammonia synthesis, the Haber and Claude processes are equivalent; (2) from the point of view of the manufacture of hydrogen, the Claude process is superior.

Mr. Claude has recently communicated to the Académie des Sciences the details of his process for the purification of hydrogen. This process is purely physical, and is based on the partial liquefaction of water gas. In the factories of the Chemical Company of Grande-Paroisse, near Montereau, Mr. Claude has installed a machine which treats 500 cubic meters of water gas per hour, giving a yield of 200 cubic meters of hydrogen. This process obviously demands motive force, but the hydrogen obtained is remarkably pure, a result which cannot be obtained by purely chemical methods of purification.

Although the results of the Oppau catastrophe are not yet known in all their details, it is difficult to make chemists believe, as the daily newspapers are saying, that the explosion was due to ammonium sulfate. This substance has not the reputation of being a powerful explosive. An ammonium nitrate storehouse has also been blamed, and this would be a more plausible explanation. It has also been said that the explosion was caused by a war explosive which was being studied. It does not seem in any case that the explosion took place in the part of the factory containing the catalyzers. Until we have further information, we may consider that the explosion was probably caused by gas, liquefied or compressed, being used apparently for ammonia synthesis.

The economic effect of this catastrophe has been the dissolution of the National Nitrogen Company. This company, which was founded by various French manufacturers, especially by the Kuhlmann establishments, was intended to develop in France the Badische Anilin patents. It had been organized for only a year, and by November 8, 1921, had to come to a decision on the development of the patents acquired by the French government.

The dissolution of this company is variously interpreted. It was thought that the Haber process, being completely ready for operation, would permit us to cover immediately our ammonia requirements and at the same time our requirements for nitric acid, since it seems more economical, at least in France, to prepare nitric acid by combustion of ammonia in a furnace, such as the Parsons furnace, the yield from such a furnace being superior in all respects to that obtained from the furnaces for the direct combination of nitrogen and oxygen in the arc. Complete inauguration of the Claude process, and especially the erection of a great number of factories, could not be completed in a short time. It is estimated that a delay of two or three years is necessary before we can be assured of a sufficient production of ammonia and nitric acid by that process.

Another lesson should be drawn from this catastrophe from the financial viewpoint. The ammonia factory at Oppau being entirely destroyed, Germany has only her Prussian factory. She will be obliged to rebuild Oppau. It is difficult to obtain the capital necessary for this reconstruction, but the interesting point is that the Badische Anilin, Bayer, Hoechster-farben, Weiler ter. Meer, Anilin Treptow, Griesheim, and L. Casella and Co., had formed, under the name of Anilin-Konzern, a group representing a value of 1,910,000,000 marks, which has established an affiliated company for industrial self-insurance, the Pallas Insurance Co. This company was of recent date and consequently had not the financial reserves necessary in the face of such a disaster. The private insurance companies held only a small share of the risks of the enterprise. The system of industrial self-insurance, which was employed to a large extent in Germany and which was developing to a greater and greater extent in France, is going to meet strong opposition on this account.

THE USE OF WHITE LEAD IN PAINT

The International Labor Conference, which is to meet at Geneva in October 1921, will consider among other questions the use of white lead in paint.

According to a preliminary report, different nations have already expressed their point of view. This can be summarized in the following conclusion: Just as provided in the French law, white lead should be prohibited as such, but it could be used, ground in oil, in paint for the exterior of houses. It is also stated that in spite of all experiments which have been made, absolutely nothing has been found which has the qualities of white lead. On the other hand, a very severe hygiene and prophylaxis is recommended for workers who use white lead. The measures suggested consist of the suppression of dust, especially that produced by dry grinding, the increase in installations of baths and lavatories, separate closets for working clothes, prohibition of eating and smoking during work, individual instruction to all workers on hygiene and health, frequent medical visits, and the obligation of the physician to report illnesses which originate with the lead paints.

THE JOACHIMSTHAL RADIUM MINES

The radium mines of Pechblende in Joachimsthal, which belonged formerly to the Austrian Empire, are now in the hands of Czechoslovakia. The government of that country has completed a contract with an English company (Imperial and Foreign Corporation) which leaves to the Czechoslovakian government the ownership and control of the mines and gives the English company authority for their development and commercial utilization. This is virtually a renting contract.

Before the war, the production of these mines was about 4 g. a year. This year it will be about 5 g., and the yield will be increased next year. Of the quantity produced annually, the Czechoslovakian government eserves 2 g. for research institutions on radioactivity.

October 11, 1921

LONDON LETTER

By STEPHEN MIALL, 175 Haverstock Hill, Hampstead, N. W. 3, England

In the September number of THIS JOURNAL were two papers, which greatly interested me, on "Motor Fuel from Vegetation" and the "Role of the Chemist in Relation to the Future Supply of Liquid Fuel." The problem of liquid fuel is one which we also have to consider and it is quite possible that during the last few months one portion of this problem has been solved.

A score of years ago a process was devised for the manufacture of a smokeless fuel called Coalite by distilling coal at a low temperature; this was widely advertised and a limited amount of this fuel was placed on the London market. It was a good fuel and well suited to the open grates which we affect here. But the plant for making this fuel was quite unsatisfactory, and the company soon found itself in financial troubles. Other forms of plant were devised and more engineering and financial disasters were encountered until Coalite and the financiers who controlled it became almost a byword. Was it not Dr. Johnson who described a second marriage as the triumph of hope over experience? This would not be an unfair description of the Coalite Company's finances. But an obstinate optimism does every now and then win through, and when I went over the company's works at Barnsley in Yorkshire in the spring of this year I thought that there was good ground for expecting their experiments would at last be successful. Their distillation at a low temperature gave them an excellent domestic fuel, a certain quantity of rich gas, a tar or oil which has a value as a fuel and may hereafter be even more valuable, and a few other by-products such as would be expected. And it seemed to me that their estimate that the operation could be carried on at a profit would probably be justified. Since then the Low Temperature Carbonisation Company has enlarged the Barnsley plant and put up more retorts and the process has been worked on a commercial scale and has been carefully watched for about four months by Sir Percy Girouard, one of the directors of Messrs. Armstrong, Whitworth & Co., the well-known engineers. The results up to date are, I understand, entirely satisfactory, and unless some unexpected disappointment appears at the eleventh hour the distillation of coal at a low temperature and on a profitable basis will be an accomplished fact by the time these notes reach you. This will be a factor of considerable importance in the gas world, to owners of coal mines and coke ovens, and to many others. The mechanical difficulties of the retorts seem to have been overcome and the company is no longer troubled by a large proportion of breeze or dust, or by the extremely friable nature of the Coalite which was at one time a source of worry.

The company claims that coals in general can advantageously be treated by this process and that a ton of an average coal will yield about 70 per cent of Coalite, 6000 cu. ft. of gas of a calorific value of about 650 B. t. u., 20 gal. of fuel oils, 3 gal. of light oils, and 20 lbs. of sulfate of ammonia.

THE VISIT OF THE SOCIETY OF CHEMICAL INDUSTRY

The small party of the Society of Chemical Industry who visited America recently have now returned to their native country and have been very much pleased by their visit. Their lack of numbers is a symptom of the difficult times in which we live and is no criterion of the interest and affection we have for our first cousins in Canada and our second cousins in the United States. The travelers seem to have had a strenuous time—a crowded hour of glorious life—and saw much to interest them and stimulate their activity. Those I have spoken to, or rather listened to, are full of praise for the excellent organization of all the details of the meetings, for the splendid hospitality they enjoyed, for the kindly spirit of coöperation displayed. You and your colleagues did all that was possible to make our party happy, though I gather from Sir William Pope that this necessitated an occasional evasion or even breach of the law. Pascal, who was not only a man of science, but also a philosopher, said that great men had the supreme pleasure of being able to make others happy and he told a young man that if he did this and no more he might lose the life eternal, but at least he would be damned like a gentleman. The American chemists can at any rate expect this consolation prize even if their trespasses disqualify them from the highest reward! But let us not look on the dark side of things; perhaps there is no more moral obliquity in a breach of the laws about prohibition than there is in poaching or smuggling, and the powers that be will doubtless take a broad view of morality. It was his gardener who secured the acquittal of one of the Scots lords from a charge of treason by a little perversion of the truth before the jury and when a friend said that at the Day of Judgment he might have to plead guilty of perjury he replied, "I would rather trust my soul to Almighty God, than my old master to those twelve scoundrels."

October 7, 1921

The National Aniline & Chemical Co., Inc., has announced the production of the following new dyes: National Niagara Blue R W, National Niagara Blue R W Conc., National Acid Fast Violet B G, National Niagara Sky Blue 6B, and National Niagara Sky Blue 6B Conc.

The American syndicate which acquired an interest in the Solvay concessions in Spain and spent several million pesetas in sinking a shaft for potash, has terminated the contract and abandoned further operations. A report from Madrid states that the trial boring put down by the Spanish government in association with the German Potash Syndicate at Cardona is to be abandoned, having reached a depth of about 1200 meters without striking either potash or rock-salt deposits.

OBITUARY

Samuel Stockton Voorhees

On the evening of September 23, at Portland, Maine, died Samuel Stockton Voorhees, Engineer Chemist of the Bureau of Standards, in the 55th year of his age. To a host of friends his passing brings personal sorrow because of loss of one endeared to them by his genial and manly qualities and deep regret that the chemical profession should be prematurely deprived of the services of a man so well informed and broadminded, whose conduct was always guided by high ideals.

Voorhees was born at Springfield, Ohio, January 15, 1867, his parents, of old American stock, being John Hunn and Elizabeth Aston (Warder) Voorhees. He studied at Lehigh University, in the class of 1888, without graduating, and then took a special course in chemistry at Columbian (now George Washington) University, in Washington, D. C. He married in 1895 Laura Toucey Kase, of Danville, Pa., who with three daughters survives.

His first professional services were with the Cambria Iron Company, at Johnstown, Pa., and the Pennsylvania Railroad, at Altoona, Pa. In the employ of the latter he had the good fortune to be associated with the lamented Dr. Charles B. Dudley, a past president of the American Chemical Society, whom he always held in grateful remembrance. He there also formed lasting acquaintance with men who have risen to prominence in the railroad world. It was with two of them and other friends that he undertook the vacation trip to the north woods of Maine, where an illness from which he had long suffered developed to such an extent that he had to be removed under great difficulties to a hospital in Portland, where within a week he underwent two operations, from the second of which he was unable to rally.

Voorhees' railroad experience was continued during 1896 to 1899 with the Southern Railway Company at Washington, D. C., and Alexandria, Va., and from 1899 to 1901 with the New York Central and Hudson River Railroad, at Albany, N. Y.

The fifteen years of practical knowledge acquired in industrial fields fitted him admirably for the government service into which he then entered and in which he remained during the rest of his life. From 1901 to 1908 he was Engineer of Tests in the office of the Supervising Architect of the Treasury Department and continued that work until 1910 after it was taken over by the Technologic Branch of the Geological Survey. In 1910 this service was transferred to the Bureau of Standards, where it has since remained.

Voorhees was at the time of his death a member of the American Chemical Society, the American Association for the Advancement of Science, the Washington Academy of Sciences, the Biological Society of Washington, the American Society for Testing Materials, and the International Association for Testing Materials. He was long a member also of the Society of Chemical Industry. In the American Society for Testing Materials he was most active, serving a term as vice president and frequently on committees, participating in the preparation of many reports. It is upon these reports and the very many that he rendered in government service that Voorhees' professional reputation chiefly rests. His long and varied experience in the fields of railroad and structural supplies gave him a practical knowledge and a grasp of the applications of those materials such as few men possess.

Associated as I was with him for over eleven years at the Bureau of Standards, where he was in charge of a section of the chemistry division, I bear glad testimony to his intense loyalty to our Government and to his unflagging zeal and industry on its behalf. To aid the Government, the public, and the industries was his constant aim. I also wish to acknowledge my own indebtedness for the strong support and wise counsel that were ever at my service. His loss left a void in the Bureau of Standards that will be hard to fill.

The social side of Voorhees was strongly developed. He was an active member of the Cosmos Club of Washington, enjoyed the company of others, and contributed to their enjoyment, whether as genial entertainer or attentive listener, always the courtly gentleman. His disposition was most kindly, and any friend or neighbor in trouble or sickness was sure of his solicitous attention. Voorhees was an ardent fisherman, and it was with evident anticipations of a good time with the finny tribe that he set out on his trip to the Maine woods. His last note to me from camp, however, raised forebodings as he told of his inability to join in the sport he so enjoyed. Peace to the spirit of a fine man and a faithful friend. W. F. HILLEBRAND

PERSONAL NOTES

Dr. J. W. Richards, of Lehigh University, died suddenly on October 12, 1921, at his home in Bethlehem, Pa., of heart trouble. Dr. Richards was born in Oldbury, England, fifty-seven years ago. He was a graduate of Lehigh University. He became an instructor in metallurgy and mineralogy at Lehigh University in 1887, assistant professor in 1897, acting professor in 1902, and was professor from 1903 until his death.

Dr. Richards had an international reputation in various branches of metallurgical technology. He was a charter member of the American Electrochemical Society, its first president in 1902 and 1903, and secretary since 1907. He was a member also of the Franklin Institute of Philadelphia, the American Chemical Society, of which he was vice president in 1899, the Faraday Society, the American Institute of Mining & Metallurgical Engineers, the American Institute of Chemical Engineers, and of other engineering and scientific societies.

Mr. Walter G. Campbell, who has been with the Bureau of Chemistry since 1907, and upon the reorganization of the Bureau in 1914 was made chief of the Eastern Food and Drug Inspection District, was recently appointed acting chief of the Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C., to succeed Dr. Carl L. Alsberg, who has been appointed director of the department of production and distribution of the Food Research Institute of Stanford University, Cal.

Prof. J. Ernest Woodland, head of the science department of Mechanics Institute, Rochester, N. Y., and a chemist of national reputation, died recently in a local hospital at the age of 55. Professor Woodland was formerly of the faculty of the University of Rochester and former chairman of the Rochester Section of the American Chemical Society.

Announcement was recently made of the death of **Mr. Lloyd W. Chapman,** who was secretary of the California Section of the American Chemical Society.

Mr. Allen Abrams has resigned as research associate from the research laboratory of applied chemistry at Massachusetts Institute of Technology to become chief chemist for the Cornell Wood Products Co., manufacturers of wall-board and box-board, Cornell, Wis.

Mr. Edward R. Weidlein has recently been appointed director of the Mellon Institute of Industrial Research, of which he has been acting director since the resignation of **Dr. Raymond F. Bacon.** Mr. Weidlein has been associated with the Institute for a number of years. He was a senior fellow from 1912–1916. In 1916 he became associated with the administrative staff as assistant director, and later as associate director. He became acting director in 1918 during the absence of Dr. Bacon who was serving in the Chemical Warfare Service.

Dr. H. E. Howe, of the National Research Council, Washington, D. C., has been made the chemical representative of the American Federation of Labor on the Advisory Committee on Disarmament, recently appointed by Mr. Gompers.

Mr. Silas Carl Linbarger, who was ceramic engineer of The Carborundum Co., Niagara Falls, N. Y., died recently at his home in that city, at the age of 29.

Mr. Harry R. Cary has left A. L. van Ameringen, dealer in perfumes and essential oils, and has purchased the drug store of James R. Spillan at Elmira, N. Y.

Mr. Earle E. Richardson who has been instructing in analytical chemistry and physics for the past four years at the Massachusetts Institute of Technology has been appointed research physicist under Mr. L. A. Jones at the research laboratories of Eastman Kodak Co., Rochester, N. Y.

Mr. Edwin R. Theis, formerly chemist for the American Oak Leather Co., Cincinnati, Ohio, has joined the staff of the department of leather research, College of Engineering and Commerce, University of Cincinnati, as research assistant.

Mr. Oliver C. Ralston has been promoted from the position of superintendent of the Mining Experiment Station of the Bureau of Mines at Seattle, to assistant chief metallurgist with headquarters at Berkeley, Cal., where he will also act as superintendent of the Pacific Experiment Station of the Bureau of Mines.

Mr. F. C. Henriques, who was chemist for the North Western Magnesite Co., assisting in the research work on magnesite at the Bureau of Mines, Berkeley, Cal., is at present chemist for the Sampson Magnesite Company, Inc., which owns and operates the mine and calcining plant at Sampson Peak, Mendota, Cal.

Mr. E. S. Crosby has resigned as sales and advertising manager of the United States and Cuban Allied Works Engineering Corp., to become manager of the Eastern District of the Celite Products Co., in New York City.

Miss Ruth E. Merling, who had charge of the chemistry courses in the summer session of College of St. Teresa, Winona, Minn., has accepted a position for the coming year as instructor in chemistry at the University of Kansas.

Dr. Ernest E. Lyder, formerly of the H. L. Doherty Co., is now with the Catlin Shale Oil Co., of Elko, Nev.

Mr. George V. Downing, formerly research chemist with the I. P. Thomas & Son Co., Paulsboro, N. J., is now located in Salem, Va., as chief chemist for Leas & McVitty, Inc., and the Buena Vista Extract Co. In this work Mr. Downing will be associated with **Mr. L. M. Whitmore**, formerly leather chemist with the Bureau of Standards, and now manager of the process department of the above concerns. They are expected to do extensive work on the use of syntans and other tanning materials.

Dr. H. E. Haggenmacher has been appointed research chemist of the Grasselli Chemical Co., Cleveland, Ohio. While in New York, Dr. Haggenmacher was connected with Collins and Roessel, Inc., engineers.

Miss Helen C. Gillette, formerly in charge of the works chemical laboratory of the Prest-O-Lite Company, Inc., at Indianapolis, Indiana, is now situated with the Union Carbide & Carbon Research Laboratories, Inc., Long Island City, N. Y.

Mr. Edward S. Liebscher has resigned as research chemist with the American Lead Pencil Co., Hoboken, N. J., and is now associated with the Far East Products Co., Inc., Brooklyn, N. Y., as president and technical director.

Mr. N. K. Chaney is in general charge of the research work of the Union Carbide & Carbon Research Laboratories, Inc., at Long Island City, N. Y. Mr. Chaney was formerly in the research laboratory of the National Carbon Co., which laboratory has been merged with that of the first-named firm.

Mr. C. S. Adams has given up his position as lecturer in chemical engineering in the University of Toronto in order to pursue his studies for a Ph.D. degree in Ohio State University, Columbus, Ohio.

Dr. Edgar F. Smith accepted an invitation from the trustees and faculty of Cornell University to speak at the laying of the cornerstone of their new chemical laboratory on October 20, at which time their new president was inaugurated. From there he went to Chicago where he had been invited to speak at the annual banquet of the American Mining Congress on the evening of October 21.

INDUSTRIAL NOTES

E. D. Winkworth has recently been made executive vice president of the Solvay Process Co., in full charge of management of the Solvay Process Company and the Semet-Solvay Co. The position is a new one, and is due to the removal of E. L. Pierce, president of the Solvay Process Company and vice president of the Allied Chemical and Dye Corporation, to the New York offices of the corporation.

Manufacture of an insulating board from bagasse has been started at the first unit of the Louisiana Celotex Co., Marrero, La., which has recently been completed at a cost of $500,000. If successful, further units will be erected as rapidly as possible, and it is hoped that within a few years a large part, if not all, of the bagasse produced in Louisiana will be used in this way. It is said that the board can be produced at less than the cost of lumber, can be used in the place of lumber for nearly all purposes, and is not subject to decay like wood.

The recently organized United States Radium Co., New York, will take over a number of the larger radium companies in this country, including the Radium Luminous Material Corporation and its subsidiaries, and the Undark Radium Mines of Colorado. The radium works and extraction plant of the Radium Luminous Material Corporation at Orange, N. J., will be continued, as well as the research laboratory of the Undark organization.

The Eastman Kodak Co. of New York has taken the first steps in its plan of reorganization and recapitalization, which has been contemplated since the settlement of the government dissolution suit. The company plans to enter a new field—the developing and printing of motion picture films—and has purchased three printing and developing laboratories: the G. M. Laboratory, Long Island City, with a capacity of 3,500,000 feet of motion picture films a week; the Paragon, Fort Lee, N. J., with capacity of 1,000,000 ft. a week; and the Sen Jacq Laboratory, Fort Lee, N. J., not yet quite completed.

The University of Iowa is to have a new chemistry building, valued at $1,000,000.

A reorganization of executive forces of E. I. du Pont de Nemours & Co. is to be put in force immediately, by which there will be four main departments with six auxiliary divisions. Certain industrial branches, including dyes, pyralin, paints and chemicals, explosives and cellulose products, are put under separate general managers, each of whom will be held responsible for results in his particular industry. Managers of these branches have been appointed as follows: cellulose products, R. R. M. Carpenter; explosives, C. A. Patterson; dyestuffs, C. A. Meade; paints and chemicals, Hunter Grubb; pyralin, C. W. Phellis. The six auxiliary departments were created to act in consulting capacity and also to serve the company as a whole: legal, J. P. Laffey, chief counsel; development, Finn Sparre, director; engineering, S. M. Pierce, chief engineer; chemical, C. L. Reese, director; service, W. B. Foster, director; advertising, C. F. Brown, director.

A French estimate puts the sugar tonnage for 1921–1922 in France at 2,800,000, the area being 107,730 hectares, an increase of 18.2 per cent but a decrease in tonnage. Germany has an estimate of 335,390 hectares and a sugar tonnage of 1,250,000, an increase of 22.48 per cent. Czechoslovakia has an estimated tonnage of 600,000; Italy, 180,000; Sweden, 150,000; Belgium, 225,000; and the Netherlands, 300,000 tons.

The board of trustees of the Ohio State University has authorized the establishment within the College of Agriculture of the Plant Institute of the Ohio State University. All members of the staff of the college interested in plant studies may be members, and all graduate students doing their major work with plants are associate members. The Institute will conduct a seminary, review the work of its graduate students and encourage research. The departments of the college chiefly concerned are: botany, horticulture, farm crops, agricultural chemistry, and soils.

The Dow Chemical Company has almost completed the plant which it is building at Midland, Michigan, for the manufacture of acetylsalicylic acid and it is expected that operation will begin within a few weeks.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Importations of Dyes and Chemicals. Report to accompany H. R. 8107 to control importations of dyes and chemicals; submitted by Mr. Longworth. House Report 330. 2 pp. August 9, 1921.

Emergency Tariff Act and Dye and Chemical Control Act Provisions extended to January 1, 1922. Report to accompany H. R. 8107; submitted by Mr. McCumber. Senate Report 259. 2 pp. August 16, 1921.

PUBLIC HEALTH SERVICE

Carbon Monoxide Poisoning in Closed Garages. Public Health Reports, **36** (September 9, 1921), 2215–19. The conclusion is reached that if a car while "warming up" should give off 1 cu. ft. of carbon monoxide per minute in a closed room 10 by 10 by 20 ft., the atmosphere would reach the dangerous concentration of 15 parts in 10,000 in 3 min.

Some Suggestions Concerning Bacteriological Diagnosis of Human Botulism. K. F. Meyer and J. C. Geiger. Reprint 665. 7 pp. Paper, 5 cents.

Antineuritic Vitamine in Skim Milk Powder. J. M. Johnson and C. W. Hooper. Public Health Reports, **36** (August 26, 1921), 2037–43.

The Growth Promoting Properties of Milk and Dried Milk Preparations. J. M. Johnson. Public Health Reports, **36** (August 26, 1921), 2044–57.

GEOLOGICAL SURVEY

Gold, Silver, Copper, Lead, and Zinc in Idaho in 1919. Mines Report. C. N. Gerry. Separate from Mineral Resources of the United States, 1919, Part I. 46 pp. Published August 11, 1921. The value of mine production of gold, silver, copper, lead, and zinc in Idaho in 1919 decreased nearly 50 per cent from the value of 1918, as shown by the following table:

	1918	1919	Increase or Decrease in 1919	1863–1919
No. of producers.	301	210	—91	...
Ore, short tons...	2,091,619	1,457,395	—634,224	...
Gold............	$702,816	$713,238	+$10,422	$132,327,023
Silver, fine ounces	9,172,340	5,579,056	—3,593,284	239,457,351
Copper, pounds..	6,533,888	3,122,763	—3,411,125	126,021,580
Lead, pounds ...	294,695,993	182,341,898	—112,354,095	6,248,386,143
Recoverable zinc, pounds........	45,161,712	15,994,229	—29,167,483	402,374,581
Total value	$36,522,158	$18,374,315	—$18,147,843	$672,459,678

Feldspar in 1919. L. M. Beach. Separate from Mineral Resources of the United States, 1919, Part II. 12 pp. Published August 12, 1921. The feldspar sold in 1919 was 28 per cent less in quantity and 13 per cent less in value than in 1918.

Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1920. Mines Report. J. P. Dunlop. Separate from Mineral Resources of the United States, 1920, Part I. 9 pp. Published August 13, 1921. The total value of the gold, silver, copper, lead, and zinc mined and sold in the Eastern States in 1920 showed a decrease of about 8 per cent from the corresponding value in 1919, as indicated by the following table.

	1919	1920	Increase or Decrease in 1920
Ore sold or treated, short tons.	1,930,411	2,418,500	+488,089
Gold........................	$7,052	$8,515	+$1,463
Silver, fine ounces...........	104,690	112,183	+7,493
Copper, pounds...............	16,596,182	17,138,675	+542,493
Lead, pounds................	4,378,000	4,003,078	—374,922
Zinc, pounds................	242,558,000	204,484,000	—38,074,000
Total value	$26,110,186	$24,014,717	—$2,095,469

Phosphate Rock in 1920. R. W. Stone. Separate from Mineral Resources of the United States, 1920, Part II. 9 pp. Published August 11, 1921. The phosphate rock sold in the United States in 1920 amounted to 4,103,982 long tons, valued at $25,079,572, an increase in quantity of 80 per cent and in value of 116 per cent over 1919.

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1919. V. C. Heikes. Mines Report. Separate from Mineral Resources of the United States, 1919, Part I. 44 pp. Published August 16, 1921. The great decrease in the mine production of gold, silver, copper, lead, and zinc in Nevada in 1919 is shown in the accompanying table; but in spite of adverse conditions eleven mining companies in Nevada paid dividends amounting to $4,307,867.

	1918	1919	Decrease in 1919	1904–1919
No of producers:				
Placers.........	54	37	17	...
Deep mines.....	660	384	276	...
Ore, short tons....	6,472,579	3,187,831	3,284,748	56,019,307
Gold[1]............	$6,619,937	$4,541,502	$2,078,435	$172,699,579
Silver,[1] fine ounces.	10,000,599	6,863,580	3,137,019	173,104,565
Copper, pounds...	116,316,441	52,331,175	63,985,266	912,516,487
Lead, pounds.....	23,316,534	15,349,370	7,967,164	200,275,171
Recoverable zinc, pounds.........	16,724,753	9,004,698	7,720,055	161,717,023
Total value	$48,528,124	$23,433,171	$25,094,953	$483,054,513

[1] Includes placer production.

Gold, Silver, Copper, Lead, and Zinc in Montana in 1919. C. N. Gerry. Mines Report. Separate from Mineral Resources of the United States, 1919, Part I. 39 pp. Published August 17, 1921. The value of the mine production of gold, silver, copper, lead, and zinc in Montana in 1919 decreased nearly 49 per cent from that of 1918. The decrease was general and pronounced, both in the quantity and value of all the metals and in the quantity of ore mined and treated.

Deposits of Chromite in California, Oregon, Washington, and Montana. J. S. Diller, L. G. Westgate and J. T. Pardee. Bulletin 725-A. Separate from Contributions to Economic Geology, 1921, Part I. 84 pp. Published August 3, 1921.

Deposits of Manganese Ore in Montana, Utah, Oregon, and Washington. J. T. Pardee. Bulletin 725-C. Separate from Contributions to Economic Geology, 1921, Part I. 143 pp. Published August 8, 1921.

Contact-Metamorphic Tungsten Deposits of the United States. F. L. Hess and E. S. Larsen. Bulletin 725-D. Separate from Contributions to Economic Geology, 1921, Part I. 65 pp. Published August 9, 1921.

Geology of the Cement Oil Field, Caddo County, Oklahoma. Frank Reeves. Prepared in coöperation with the Office of Indian Affairs. Separate from Contributions to Economic Geology, 1921, Part II. 45 pp. Published August 10, 1921.

Ground Water for Irrigation near Gage, Ellis County, Oklahoma. D. G. Thompson. Water-Supply Paper 500-B. 53 pp. 1921.

Slate in 1919. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources, 1919, Part II. 7 pp.

Surface Water Supply of the United States 1918. Part V—Hudson Bay and Upper Mississippi River Basins. N. C. Grover and W. G. Hoyt. Prepared in coöperation with the States of Minnesota, Wisconsin, Iowa, and Illinois. Water-Supply Paper 475. 153 pp. 1921.

Surface Water Supply of the United States 1918. Part VI—Missouri River Basin. N. C. Grover, W. A. Lamb and Robert Follansbee. Prepared in coöperation with the States of Colorado, Montana, and Wyoming. Water-Supply Paper 476. 266 pp. 1921.

Deposits of Manganese Ore in Montana, Utah, Oregon, and Washington. J. T. Pardee. Bulletin 725-C. Separate from Contributions to Economic Geology, 1921, Part I. 103 pp. Published August 8, 1921.

Silica in 1919. L. M. Beach. Separate from Mineral Resources of the United States, 1919, Part II. 2 pp. Published August 27, 1921. The output of silica decreased 8 per cent in quantity and increased less than 1 per cent in value in 1919 as compared with 1918.

Bauxite and Aluminium in 1920. J. M. Hill. Separate from Mineral Resources of the United States, 1920, Part I. 8 pp. Published August 31, 1921. The domestic bauxite mined and marketed in 1920 showed an increase of 38 per cent in quantity and nearly 48 per cent in value as compared with the production in 1919.

The value of primary aluminium produced in the United States in 1920 was about 7 per cent greater than in 1919 and a little greater than in 1918.

Sand-Lime Brick in 1920. Jefferson Middleton. Separate from Mineral Resources of the United States, 1920, Part II. 2 pp. Published August 24, 1921. The production of sand-lime brick in 1920 continued to increase from the low output of 1918. Though the quantity was smaller than in any other year since 1911 (except 1918 and 1919) the value was the highest recorded.

Fuller's Earth in 1920. Jefferson Middleton. Separate from Mineral Resources of the United States, 1920, Part II. 2 pp. Published August 25, 1921. The output of fuller's earth in 1920 was the largest recorded; it was greater than that of 1919 by 21 per cent, more than three times as great as the output of 1913, and nearly 19 times as great as that of the first year of production.

Asphalt and Related Bitumens in 1920. K. W. Cottrell. Separate from Mineral Resources of the United States, 1920, Part II. 9 pp. Published August 25, 1921. The sales of native asphalt and related bitumens in the United States in 1920 showed an increase of 125 per cent in quantity and of about 78 per cent in value over 1919. The sales of manufactured asphalt obtained from domestic petroleum increased 14 per cent in quantity and 37 per cent in value. The sales of asphalt manufactured in the United States from Mexican petroleum increased 55 per cent in quantity and 85 per cent in value.

Gypsum in 1920. R. W. Stone. Separates from Mineral Resources of the United States, 1920, Part II. 10 pp. Published August 31, 1921. In 1920, for the first time, the total quantity of gypsum produced in the United States in a single year exceeded 3,000,000 tons. The value of the product marketed also was much greater than in any previous year.

Magnesium in 1920. R. W. Stone. Separate from Mineral Resources of the United States, 1920, Part I. 4 pp. Published August 18, 1921. So far as has been learned by the Geological Survey, only two companies in the United States produced magnesium in 1920. However, the quantity and value of the metallic magnesium reported to the Geological Survey as produced in 1920 was only slightly less than in 1919.

Surface Water Supply of the United States, 1917. Part IX. Colorado River Basin. N. C. Grover, Robert Follansbee, C. C. Jacob and C. E. Ellsworth. Prepared in coöperation with the States of Arizona, Nevada, Utah, and Wyoming. Water-Supply Paper 459. 192 pp. 1921.

Surface Water Supply of the United States, 1917. Part X. The Great Basin. N. C. Grover. C. C. Jacob, H. D. McGlashan, F. F. Henshaw, G. C. Baldwin and Robert Follansbee. Prepared in coöperation with the States of Utah, Nevada, California, Oregon, and Wyoming. Water-Supply Paper 460. 277 pp. 1921.

Copper in 1919. General Report. H. A. C. Jenison. Separate from Mineral Resources of the United States, 1919, Part I. 78 pp. Published September 8, 1921. The salient features of the copper industry for the year 1919 were the continued shortage and inefficiency of labor, the reaction from the war as reflected in a poor and very unsettled market, and the difficulties of railroad transportation. Smelter production decreased 32.6 per cent and refinery production decreased 25.8 per cent. Domestic consumption declined 44.97 per cent and the stocks of raw and refined copper reached a figure greater than ever before in the history of the industry.

Cement in 1919. E. F. Burchard. Separate from Mineral Resources of the United States, 1919, Part II. 18 pp. Published September 21, 1921. After marked declines in the output of hydraulic cement during the war years 1917 and 1918, production and shipments of cement showed satisfactory gains during 1919 (13.7 and 20.7 per cent, respectively, over 1918), and the cement industry in general made progress toward better conditions.

Platinum and Allied Metals in 1920. J. M. Hill. Separate from Mineral Resources of the United States, 1920, Part I. 14 pp. Published September 9, 1921. The platinum recovered in 1920 was about 10 per cent less than in 1919, but the palladium recovered in 1920 was about 13 per cent more than in 1919. As nearly as can be estimated, about 13,243 oz. of the new metals recovered in 1920 were derived from domestic materials.

Arsenic, Bismuth, Selenium, and Tellurium in 1920. V. C. Heickes. Separate from Mineral Resources of the United States, 1920, Part I. 22 pp. Published September 22, 1921. The sales of arsenic in the form of arsenious oxide in 1920 showed a noteworthy increase. They amounted to 11,052 short tons, valued at $2,021,356, and exceeded all former annual sales. In 1919 the sales were 6,029 tons, estimated at $1,181,684 in value.

The output of domestic bismuth in 1920 is known to have been much smaller than in 1919, but no figures can be given, as the producers object to having their output published.

The output of selenium in 1920 was 92,141 lbs., valued at $175,508, compared with 60,025 lbs., valued at approximately $125,966 in 1919. A large part of the selenium produced in 1920 was used at glass works and little of it remained in stock.

Tellurium in the form of metal was produced in 1920 at the Raritan Copper Works, Perth Amboy, N. J. The company has a stock of the metal on hand and finds no demand for the element except for use in experiments.

Abrasive Materials in 1919. L. M. Beach and A. T. Coons. Separate from Mineral Resources of the United States. 1919, Part II. 6 pp. Published September 16, 1921. This article is concerned with natural and artificial abrasives composed of one or more minerals and used for grinding, polishing, and other abrasive operations. The total value of all abrasive materials, exclusive of feldspar and various forms of quartz, consumed in the United States during the years 1915–1919 is given in the following table:

	1915	1916	1917	1918	1919
Natural abrasives..	$1,218,508	$1,664,339	$2,385,165	$2,864,332	$2,887,902
Artificial abrasives..	2,248,778	2,935,909	8,137,242	6,940,000[1]	5,019,779[2]
Imports.....	540,783	555,850	812,303	1.187,632	2,237,077
	4,008,069	5,156,098	11,334,710	10,991,964	10,144,758[2]

[1] Estimated and not including entire production during second half of 1918.

[2] Not including production of one large company.

Peat in 1920. K. W. Cottrell. Separate from Mineral Resources of the United States, 1920, Part II. 3 pp. Published September 7, 1921. The quantity of peat produced for fertilizer and fertilizer ingredient increased more than 8000 tons and for stock food more than 2000 tons, but the quantity reported as dug for fuel fell off more than 7000 tons, so that the net gain in production was only 4007 tons. On account of the higher prices, the total value of the peat sold increased more than $200,000 and was greater than in any preceding year except 1918.

Fluorspar and Cryolite in 1920. H. W. Davis. Separate from Mineral Resources of the United States, 1920, Part II. 16 pp. Published September 20, 1921. Although prices of fluorspar were somewhat lower in 1920 than in 1919 and 1918, the industry apparently enjoyed a very satisfactory year. The demand was good throughout the year except in January and December, and at times little material was available for delivery even at attractive prices.

The following table shows the amount of cryolite shipped from Greenland, which is the only place where it occurs in commercial quantities, and imported into the United States:

		Imports into United States[2]		
Year	Total Shipped Long Tons[1]	Quantity Long Tons	Value	Average Value per Ton
1913..........	10,248	2,559	$52,557	$20.54
1917..........	9,482	4,383	218,500	49.86
1918..........	9,955	1,950	97,500	50.00
1919..........	6,265	2,131	106,956	50.19
1920..........	(3)	3,864	193,638	50.11

[1] The mineral industry of the British Empire and foreign countries: Aluminum and bauxite; Imperial Mineral Resources Bureau (London), 1921.

[2] Bureau of Foreign and Domestic Commerce.

[3] Not available.

Graphite in 1920. L. M. Beach. Separate from Mineral Resources of the United States, 1920, Part II. 6 pp. Published September 16, 1921. In 1920 natural graphite was produced by 17 firms, operating in 9 different states. The total sales of domestic graphite amounted to 9510 short tons, valued at $626,202, an increase in quantity of 28 per cent and a decrease in value of 20 per cent as compared with 1919.

Fuel Briquets in 1920. W. F. McKenney. Separate from Mineral Resources of the United States, 1920, Part II. 3 pp. Published September 19, 1921. The fuel-briquetting industry made rapid strides during the year 1920 and produced a record output. The total production of briquets was 567,192 net tons, which, as compared with 1919, a year of marked depression, was an increase of 92 per cent and which exceeded the previous high record, set in 1918, by 89,957 tons. This increase was made possible by the shortage and consequent high prices of raw coal.

Strontium in 1920. G. W. Stose. Separate from Mineral Resources of the United States, 1920, Part II. 3 pp. Published September 17, 1921. No strontium ore was mined in the United States in 1920. Strontium salts were made from strontium ore at only two plants in the United States in 1920. The quantity of strontium ore imported was considerably greater than in any previous year.

Lime in 1919. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1919, Part II. 14 pp. Published October 6, 1921. The lime sold in the United States in 1919 showed an increase in quantity of 4 per cent and in value of 10 per cent, compared with 1918. The greatest quantity of lime sold in any one year was recorded in 1916; the highest mark in value was reached in 1919. The average value per ton of lime increased nearly 6 per cent over 1918 and 122 per cent over 1915.

Sodium Compounds in 1920. R. C. Wells. Separate from Mineral Resources of the United States, 1920, Part II. 12 pp. Published September 30, 1921. As indicated by the following table, the year 1920 was a good one for most sodium compounds, whether the comparison is made by tons or by dollars.

Sodium Compounds Sold in the United States, 1917–1920

Year	Quantity Short Tons	Value
1917........	10,123,322	$130,694,458
1918........	9,997,310	134,594,154
1919........	9,166,581	118,836,347
1920........	9,899,448	139,252,477

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, June 1921. W. W. Adams. 22 pp. Paper, 5 cents. 1921.

Petroleum Laws of All America. J. W. Thompson. Bulletin 206. 645 pp. Paper, 40 cents. This bulletin contains the petroleum laws of (1) United States; (2) the several oil-producing States; (3) Canada; (4) Mexico; (5) the Republics of Central and South America.

Oil-Camp Sanitation. C. P. Bowie. Technical Paper 261. 32 pp. Paper, 10 cents.

Coke-Oven Accidents in the United States during the Calendar Year 1920. W. W. Adams. Technical Paper 293. 32 pp. Paper, 5 cents. Accidents at coke ovens during the calendar year 1920 reported to the Bureau of Mines by operating companies caused the death of 49 and the injury of 3415 employees, a decrease of 4 fatalities and 616 injuries as compared with the record for 1919.

Relation of Drilling Campaign to Income from Oil Properties. W. W. Cutler and W. S. Clute. Reports of Investigations. Serial No. 2270. 11 pp. Issued August 1921.

Recent Articles on Petroleum and Allied Substances. E. H. Burroughs. Reports of Investigations. Serial No. 2271. 18 pp. Issued August 1921.

Fourth Semi-Annual Motor Gasoline Survey. N. A. C. Smith. Reports of Investigations. Serial No. 2272. 9 pp. Issued August 1921. The fourth semi-annual motor gasoline survey, conducted during the month of July, shows an interesting relation between the market price and the quality of motor gasoline. This is particularly evident if figures obtained to-day are compared with those of a year ago. At the time the Bureau of Mines conducted its summer survey of motor gasoline last year, the average tank wagon price of gasoline was 28.2 cents per gal. This year it was 21.2 cents, a drop of practically 25 per cent. In spite of this drop in price, the quality of gasoline to-day is much better than it was last summer.

Compressed Air Operated Ventilation Doors in Arizona Copper Mines. E. D. Gardner. Reports of Investigations. Serial No. 2273. 2 pp. Issued August 1921. The article is accompanied by a sketch showing a compressed air operated ventilation door.

Relation of Lead Poisoning in Utah to Mining. A. L. Murray. Reports of Investigations. Serial No. 2274. 7 pp. Issued August 1921.

Rock Strata Gases in Mines of the East Tintic Mining District, Utah. G. E. McElroy. Reports of Investigations. Serial No. 2275. 3 pp. Issued August 1921.

Investigations of Zirconium with Especial Reference to the Metal and Oxide. Historical Review and Bibliography. J. W. Marden and M. N. Rich. Bulletin 186. Mineral Technology 25. 152 pp. Paper, 25 cents. The bulletin is divided into four parts: (1) Historical review of the chief minerals, the salts of zirconium, and zirconium metal; (2) experimental data on zirconium; (3) furnaces used; (4) bibliography of zirconium and its compounds.

Pressure-Volume Deviation of Methane, Ethane, Propane, and Carbon Dioxide at Elevated Pressures. G. A. Burrell and G. W. Jones. Reports of Investigations. Serial No. 2276. 6 pp. Issued August 1921.

BUREAU OF STANDARDS

Testing of Thermometers. Circular 8, 3rd Ed. The previous edition of this circular contained, in addition to the testing regulations, much general information on thermometry and temperature measurements. The present edition has been very much shortened by including only the information which is essential to those who avail themselves of the Bureau's testing facilities. The Bureau's standard scale of temperature is defined, and the method of reproducing it is briefly indicated. A new feature of the circular is the inclusion of definite test requirements and of tolerances as to correctness of graduation.

Metallographic Testing. Circular 42, 2nd Ed. The circular discusses briefly the conditions which affect the properties of metallic materials under the following headings: microscopy and structures, thermal analysis and heat treatment, mechanical workings of metals, chemical metallurgical factors, and conditions of melting.

The Structure and Related Properties of Metals. Circular 113. In the discussion of the methods for revealing the structure of metals, the various reagents used in the macroscopic study of metals are described, particularly as related to the purpose for which they are all used; that is, for revealing chemical unhomogeneity, crystalline heterogeneity, physical unsoundness, and mechanical non-uniformity. The principles underlying the action of etching reagents are discussed and a list of suitable reagents for revealing the microstructure of the common industrial metals and alloys given.

Preparation of Galactose. E. P. Clark. Scientific Paper 416. The yield of this crude sugar is about 27 per cent of the lactose used in its preparation. The yield of the purified product is generally 82 to 83 per cent of the crude sugar taken.

The Design of Atmospheric Gas Burners. W. M. Berry, I. V. Brumbaugh, G. F. Moulton and G. B. Shawn. Technologic Paper 193. In order to understand the various factors entering into the design of burners it was found necessary to study the theory of flow of gas through different types of orifices, the principles governing the rate of injection of air into the burner, the design of the injecting tube, the rate of consumption of burners of different port areas, and the effect of adjustment of the air shutter.

Zinc Cyanide Plating Solutions. William Blum, F. J. Liscomb and C. M. Carson. Technologic Paper 195. Satisfactory zinc deposits can be secured from either sulfate or cyanide solutions, but the latter possess the advantage of "throwing" the deposit better into deep depressions or upon the surface of irregularly shaped articles. The cyanide solutions were, therefore, given first consideration in this paper.

High Fire Porcelain Glazes. H. H. Sortwell. Technologic Paper 196. This work consists of the investigation of a wide range of high fire porcelain glazes of the Seger cone formula type to determine the limits wherein lie glazes suitable for high fire porcelain, chemical porcelain, spark plugs, pyrometer tubes, etc., maturing at temperature of from Seger cones 12 to 16. The field was studied from the standpoint of fusibility and of commercial acceptability as glazes.

The Cementing Qualities of the Calcium Aluminates. P. H. Bates. Technologic Paper 197. Published October 1921. Paper, 10 cents.

Precision Test of Large Capacity Scales. C. A. Briggs and E. D. Gordon. Technologic Paper 199. Published October 1921. Paper, 5 cents.

The Production of Liquid Air on a Laboratory Scale. J. W. Cook. Scientific Paper 419. Published October 1921. A sketch is included in the paper which shows the complete air cycle through the various apparatus used in connection with a Hampson liquefier. While the paper contains little that is novel, it supplies information which does not appear to be readily accessible.

The Testing of Rubber Goods. Circular 38, 4th Ed. Paper, 20 cents. Published October 1921.

How to Get Better Gas with Less Natural Gas in Domestic Gas Appliances. Circular 116. Paper, 5 cents. Published October 1921. This paper gives the principal conclusions from the laboratory and field investigations of the Bureau of Standards on the correct use of natural gas in the home. It is estimated that it would take a million dollars worth of artificial gas each day to replace the waste in natural gas appliances.

COMMERCE REPORTS

Preliminary figures of **crude-oil** imports into the United States for July give the amount as 337,968,176 gal., which is a marked decrease from the June figures. (P. 18)

The tax on Mexican **crude oil** is now so great that it is equal to or greater than the market value of the oil at the well. (P. 18)

The following tabular statement gives statistics of Mexican **mineral production** for the year ending June 30, 1921:

	Pounds
Gold	22,972
Silver	2,033,129
Copper	101,538,043
Lead	267,716,152
Zinc	31,665,104
Quicksilver	170,261
Antimony	3,466,475
Graphite	6,418,777
Tungsten	76,983
Tin	3,501
Arsenic	2,642,890
Manganese	1,848,849

(P. 23)

The demand for **paints** and **varnishes** in Argentina is fair, and the percentage of these products coming from the United States has increased greatly. (P. 25)

American **paints** and **varnishes** now occupy a very favorable position in the Bolivian market, supplying more than 50 per cent of all paints and varnishes imported. Before the war Germany held first place in this market, and as soon as it is again in a position to supply these articles it will be a strong competitor of the United States. (P. 26)

The **paint** industry of Bahai has not developed to any great extent and it furnishes a very good market for American paints. (Pp. 26–7)

Attention is called to the possibilities of **alfa,** which covers several million hectares in Algeria, for paper making. Analysis shows it to give 50 per cent of its weight in cellulose. **Kaolin** is also found in Algeria in large quantities. (P. 28)

Experiments by the Forest Products Laboratory at Perth, West Australia, for ascertaining the paper-making possibilities of certain hard woods indicate that these **hardwood papers** are much stronger in almost every respect than a series of imported good office envelope and bond papers taken at random from the laboratory stock. (P. 29)

A recent discovery was made of Canadian **asbestos-bearing rock** which gives promise of being of considerable commercial value. (P. 29)

An excellent showing of very **light oil** has been discovered in the Philippine Islands. (P. 41)

Business in **chemicals** and **dyes** in the United Kingdom has been scarce for many months, these trades being greatly affected by the depression in the textile and paper-making industries. (Pp. 49–50)

The pronounced stagnation of the past few months in the **vegetable-oil** trade at Marseilles has terminated and prices are moving upward vigorously. This is particularly true with respect to copra oil. (P. 68)

The consumption of **petroleum** in Chile is rapidly increasing, as many of the country's large industries are converting their coal-burning power plants into oil burners, and others are using electric power derived from the use of Diesel engines in connection with generators. This oil is supplied by the United States, Mexico, and Peru. (Pp. 78–9)

The Dominican Republic offers a steady and favorable market for the sale of American **paints** and **varnishes.** There is no local industry, all the supplies used being of foreign origin. (P. 83)

Finland's **paper** and **pulp** industries are reviewed. (Pp. 89–92)

Petroleum is at present the most important export of Poland. The following table shows the annual statistics of production and of wells in process of drilling for the years 1909–1920, the production of the oil fields having reached their maximum in 1909:

	Production		Number of Wells Being Drilled at End of Period
Years	Quantity in Metric Tons	Per cent of 1913 Production	
1909	2,086,000	182	216
1910–1912 (average)	1,437,000	126	316
1913	1,144,000	100	286
1914–1918 (average)	817,000	71	(1)
1919	832,000	73	167
1920	765,000	67	221

[1] No data.

(Pp. 109–10)

The Esthonian **paper** industry is experiencing difficulty in obtaining adequate stocks of raw materials in connection with the paper industry. (P. 89)

The Polish government has made special efforts at organizing and exploiting the production of **salt,** with the result that in 1920 an average monthly production of 27,000 tons was attained. (P. 110)

According to expert opinions obtained by the Geological Commission of Finland, the deposits of **iron ore** in the Porkonen-Pahtavaara region of Kittila, estimated to contain 100,000,000 tons of ore, cannot be utilized for the next ten years, because of the high percentage of phosphorus and the difficulty of separating it from the ore and because of the inaccessibility of the mines. (P. 129)

Dutch trade in **oils** and **fats** is reviewed. (Pp. 152–3)

French **chemical industries** show a remarkable development in those industries for which it, like other countries, was dependent on Germany before the war. The same is true of British chemical industries, especially in the coal-tar products and dyestuffs. (P. 161)

A factory for the manufacture of **phosphorus** is to be opened in Sao Jeronymo. (P. 171)

Recent experiments with Brazilian **pyrites** in the manufacture of sulfuric acid have given the most satisfactory results, it being claimed that the national product is not only much cheaper than that imported from the United States but superior, especially in the production of sulfur. (P. 171)

Owing to depreciation in the values of metals last year, practically all **mining operations** in the Torreon District, Mexico, are at a standstill. (P. 171)

The use of **fertilizers** in Ceylon and the extent to which they are used are described. (Pp. 173–4)

The excise duties on **petroleum** in the Netherlands East Indies have been increased by an ordinance of May 13, 1921. (P. 182)

China's exports of **bean oil** from Dairen this season are estimated to have been only 33$^1/_3$ per cent of normal. The trade in **sesamum seed oil** also notably decreased. (P. 190)

The German Minister of Economics is making an investigation of the **chemical industry.** He has received reports from 18 important corporations representing the principal branches of the industry, in almost all of which particular emphasis is laid on the difficulties arising out of the operation of the sanctions provided by the treaty of Versailles. Exportation has almost entirely ceased except for products in which Germany has specialized. The only branch of the chemical industry which is at all prosperous is that occupied in the manufacture of **fertilizer.** (P. 198)

The manufacturers of **coal-tar products** are said to be the only German chemical manufacturers who have been able to keep their foreign markets, but even the marked fall in the price of raw materials has not been sufficient to induce these factories to increase their output or to manufacture stocks. (P. 198)

In the German **lignite** industry it has been necessary to lay off workmen on account of a lack of markets. There is a stock of **paraffin oil** on hand amounting to 20,000 tons. (P. 198)

The Chilean **iodine** industry, which is controlled by a combination, is reviewed and the objects of the combination are defined. (Pp. 198–9)

Chemicals in the trade of British Malaya are described, among which are mentioned turpentine, chloroform, red lead, hematite, sulfur, latex, Paris green, etc. (P. 199)

In a review of the sale of **medicinal drugs** in Chile it is stated that there is hardly a branch of the Chilean import trade which is more important in volume, more generally distributed, or more profitable than that of drugs and medicinal preparations. According to the official statistics of 1919, more than 95 per cent of these imports come from the United States. (Pp. 199–201)

The German **Potash** Syndicate has secured permission to increase the price of potash by an average of 35 per cent. This additional increase will be distributed as follows:

Kinds	Estimated Sales Metric Tons	Previous Prices Marks	Percentage of Increases Per cent	New Prices Marks
Carnallite	2,402	76.5	30	99.0
Kainite	210,744	90.0	30	117.0
20 per cent kainite	54,576	111.0	32	146.0
30 per cent kainite	24,331	124.5	36	169.0
40 per cent kainite	239,392	150.5	37	205.5
Chloride of potassium				
50 per cent	124,218	172.5	37	236.0
60 per cent	36,843	189.0	37	259.0
Sulfate of potassium	4,241	228.0	40	319.0
Magnesium	3,252	250.5	40	350.0

(Pp. 201–2)

German manufacturers have largely regained control of the Mexican market for **aniline dyestuffs** and dry colors and indications point to the early reëstablishment of their former supremacy in this field. (P. 202)

Natural **soda** produced in Central Africa is being imported into Japan after being refined and has come into demand in consequence. Caustic soda made from this natural soda compares favorably with other makes. (P. 202)

A strong movement is taking place in Cuba to replace **gasoline** with alcohol as the motive power for self-propelled vehicles. (P. 205)

Benzene, which in Germany is used in place of gasoline, is unquestionably the most interesting single factor tending to revolutionize the post-war German petroleum market. The benzene production in 1920 amounted to 150,000 tons, and while this is more than 30,000 in excess of pre-war production, it is still about 100,000 tons below the average yearly production during the war. The sale of this coal-tar by-product, while still nominally under government control, is without restriction and is retailed at the price of 5.60 marks per liter. (P. 206)

A noticeable decrease is evident in the German consumption of **illuminating oil** as compared with 1913. The German consumption of this product in 1913 amounted to 750,000 metric tons but fell in 1920 to about 120,000 metric tons, the greater part of which was imported from the United States. (P. 206)

Oil is the principal fuel of the nitrate region of Chile, having largely replaced coal and will completely replace it unless better methods of handling and selling coal are put into effect. (P. 207)

A demand for **benzene** is reported in Japan. (P. 207)

Discovery of a large area of **petroleum-bearing schist** or shale has been made at Chucumata, Chile. (P. 207)

The Dominican Central Railway will hereafter use **oil as fuel** instead of coal. (P. 207)

STATISTICS OF EXPORTS TO THE UNITED STATES

RUSSIA—(P. 42)
Licorice root
Potassium carbonate
Platinum

FINLAND—(P. 92)
Cellulose

DANZIG—(P. 119)
Chemicals
Mineral wax

BOOK REVIEWS

Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. Issued by the Society of Chemical Industry. Volume V, 1920. 640 pp. Society of Chemical Industry, Central House, 46–47 Finsbury Square, London, E. C. 2, England, 1920. Price, to members, 8s. 3d. post free; non-members, 15s. post free.

The Society of Chemical Industry has now issued Volume V, 1920, of its Annual Report on the Progress of Applied Chemistry. The volume contains twenty-five reports by authorities in as many fields of industrial chemistry; and in addition there is a chapter on "Plant and Machinery" and one on "Analytical Chemistry."

The various reports are not only summaries of the year's progress, but are interestingly written and include discussions of advances made in various parts of the world. Reference is made to patents as well as to original articles in all cases. Statistics are used to good advantage. The completeness of the several reports is indicated by the headings in the chapter on India rubber. Following a short introduction and a paragraph on statistics there are several pages on the important subject of raw rubber production. Then vulcanization, accelerators, compounding ingredients, aging of raw and vulcanized rubber, the stress-strain curve, and analytical processes follow in order. A deal of information is crowded into the eighteen pages devoted to the subject.

The discussion of "coloring matters and dyes" (32 pages) should be read by any unconvinced of the necessity of firmly establishing that industry here. The conclusion is stated as follows (page 92):

> Arguments based on the respective national values of the dye industry and the textile industry were rather puerile, for by this time it appears that all are agreed that the permanent establishment of the former is essential to our national safety, and that this must be accomplished with as little injury as possible to the interests of the latter, as we receive from that source such a large proportion of our national income.

Those who wish to keep well informed in many fields will find the volume a handy encyclopedia. Interesting notes on accomplishments which escape all but the specialist abound. Thus we read of a novel method for dislodging dust electrostatically deposited, wherein a siren or whistle is used to set up sound waves of sufficient intensity to do the work. The katharometer for quickly testing the purity of gases from a very small sample receives notice. The formation of the Section of Cellulose Chemistry in the AMERICAN CHEMICAL SOCIETY is cited as one evidence of increasing interest in the subject.

Much space is properly given to fuel in its various phases. One author regards the rational treatment of coal as the most promising source of motor fuels, and the Gas Regulation Act of 1920 is regarded as the outstanding feature of the year in the field of rational fuel utilization. This Act does away with the antiquated candlepower specifications, and substitutes a commercial heat unit known as the therm, which is set as equal to 100,000 B. t. u. It is to be regretted that equal advances have not been made in our own country. The authors of the chapter on fuel state "There are small grounds for hope that the days of cheap and abundant fuel are to return. The coal consumer's most effective remedy would therefore seem to be to meet dearness and scarcity by economy in consumption."

There is nothing which competes with these Annual Reports, and they are to be highly recommended. The volume should find a place in more American libraries. There is a subject and a name index and an extensive list of abbreviations used in footnotes. The headings of the chapters are given here to indicate the scope of the work to those interested in knowing to what extent their own specialty may be represented:

Plant and Machinery; Fuel; Gas, Destructive Distillation, Tar Products; Mineral Oils; Coloring Matters and Dyes, Fibers, Textiles, Cellulose, and Paper; Bleaching, Dyeing, Printing, and Finishing; Acids, Alkalies, Salts, etc.; Glass; Refractory Materials; Ceramics and Building Materials; Iron and Steel; Metallurgy of the Nonferrous Metals; Electrochemistry; Oils, Fats, and Waxes; Paints, Pigments, Varnishes, and Resins; India Rubber; Leather and Glue; Agricultural Chemistry; Sugars, Starches, and Gums; Fermentation Industries; Foods; Sanitation and Water Purification; Fine Chemicals, Medicinal Substances, Essential Oils; Photographic Materials and Processes; Explosives; Analytical Chemistry.

H. E. HOWE

Lubricating and Allied Oils. A Handbook for Chemists, Engineers and Students. By ELLIOTT A. EVANS, Chief Chemist to C. C. Wakefield & Co., Ltd. xx + 129 pp. Chapman Hall, Ltd., London, 1921. Price, 9s. 6d. net.

In an editorial note on the D. U. (Directly Useful) Technical Series to which the present book belongs, it is explained that "theoretical books have been written more for the training of college students than for the supply of information to men in practice, and have been greatly filled with descriptions of an academic character. Practical books have often sought the other extreme, omitting the scientific basis upon which all good practice is built, whether discernible or not. The present series is intended to occupy a midway position." The author was urged to write this book as an aid to chemists in the examination of lubricating oils, and in the drawing up of specifications for them, while the engineer is given instruction about their properties and use, and is taught how to interpret specifications. This is quite a task to accomplish in a book of 122 octavo pages, exclusive of index. Credit is due the author for what he has succeeded in doing, though in many respects the book leaves much to be desired.

In the first four pages the history of petroleum, from the use of "slime" (bitumen) in building the Tower of Babel to present-day prospecting in England, is discussed. The second chapter of two pages takes up the refining of petroleum. Next follows a historical account of the fatty oils, and a peep into the future when we shall have to use most of our rape and castor oil for the production of margarine. After listing the principal oil-bearing seeds, the oils from marine animals are taken up, particularly cod-liver, shark, whale, porpoise-jaw and porpoise-blubber oils. The solid fats are not mentioned.

After the first ten rather sketchy pages, the interesting part of the book commences. The interest lies not in the very explicit and detailed directions for laboratory tests, but in the unusual information, for which one would not look in a book of this size. For instance, several pages are given to the calculation of the flash points of mixtures of known oils and to a discussion of the conditions which must be considered when using flash-point apparatus.

Perhaps the best example of the lack of balance in the book is the giving of nearly eight pages to the subject of specific heat, with two methods for its determination and several tables of specific heats of different series of hydrocarbons. Yet nowhere in this chapter, or elsewhere in the book, is the reader told what use can be made of this information.

Chemical methods are described in the fifth and sixth chapters, a total of 34 pages. Under the heading, "Gumming Test," Gill's method with nitrosulfuric acid is dismissed with the remark, "this test is of little value." The author prefers an oxidation test similar to the usual sludging tests for transformer oils.

The "coke value" of oils for internal combustion engines is found by burning off a 5-gram sample in a platinum dish. This description of the method is enough to condemn it. Indeed, the author concludes from the results of engine trials that "it is reasonably certain that the coke value and similarly obtained values are unreliable."

Of the many oxidation tests for transformer oils, the author prefers "the sludge test which was designed by Michie and standardized in detail" by the Insulating Oil Committee. This, "whilst being extremely useful, and probably the best yet designed for its purpose, is not clearly understood. That it is an oxidation test is certain, but what it is in the oil which oxidizes is not certain." The author does not believe that "the sludging qualities of an oil can be measured by its iodine value," as claimed by Radcliffe. He thinks that color is no criterion of the liability to form sludge. The reviewer is in entire accord with both of these views.

Chapter VII, on the oxidation of petroleum, contains much of interest. The author might well have continued along the same line for the succeeding four pages, instead of practically wasting the space on a chapter entitled "Oleography." "The oleograph test consists in placing a drop of oil on a perfectly clean surface of water, and noting the configuration of the film produced. Each oil produces a design peculiar to itself under definite conditions, hence any oil can be identified by noting the design produced when a drop of the oil is placed on water."

Chapter IX, on the selection of lubricants, is one of the most satisfactory in the book. The next chapter, on "Oils Employed," is also readable, except for a three-page table which lists "the most suitable grades of Wakefield 'Castrol'" for 205 different makes of automobiles. This savors too much of advertising, for the author is chief chemist to this Company.

To sum up: The book is unevenly written as regards the space given to some of the topics and the selection of others which might well have been omitted; the author is occasionally ungrammatical and does not always write clearly; the proofreading was carelessly done. In spite of these faults the book is, on the whole, worth having.

C. E. Waters

La Chimie et La Guerre. By Charles Moureu. 377 pp. Maison et Cie., 120, Boulevard Saint-Germain, Paris, France, 1920. Price, 10 fr. net.

In this book, Professor Charles Moureu has, with unusual success, depicted the great role which chemistry has played during the past war. Not content with limiting his work to the use of toxic chemicals in war, Professor Moureu has considered the metallurgical, explosive, aeronautical, camouflage and food problems, and also the general problems incident to supply and the medical care of an army and nation at war, all from a chemist's point of view. The entire work is replete with statistics, and apparently Professor Moureu has been very careful to give credit to whom credit is due in outlining work on war problems.

A review of the part which French chemists played in the war is shown in a very clear and comprehensive study of the organization effected by French chemists. The various problems incident to the war are taken up in considerable detail and a review of them recalls to the reader's mind the great debt which this country owes to France for supplying necessary technical assistance and, particularly, munitions at a time when this country had not met the requirements of its program. As shown by Professor Moureu, 940,000 gas shell of various calibers were supplied to the American Army.

In his chapter on "Chemistry and the Lessons of the War," Professor Moureu has carefully considered the means as well as the necessity for training chemists. He also considers the relation which exists between pure and applied research. In a most interesting manner, he brings up the problem of maintaining the cordial spirit of coöperation in peacetime that existed during the war between scientists of the various allied Powers.

One cannot, in a brief review of this book, mention all its points of interest. The consideration of the German chemical problems is probably one of the most interesting articles of its kind in print. The parts of this book which cover the work of the French Chemical Warfare Service would give anyone unfamiliar with this organization a clear view of its many problems and the competent manner in which they were handled. This applies not only to the problems of mobilization, research, and production, but also to problems which occurred in the field.

I am thoroughly convinced that Professor Moureu's book is a valuable addition to the literature of war and will prove highly interesting and instructive to anyone who may be interested in some of the national aspects of the application of chemical knowledge.

Amos A. Fries

Tables of Refractive Indices. II—Oils, Fats and Waxes. Compiled by R. Kanthack. Edited by J. N. Goldsmith. Demy 8 vo. 295 pp. Adam Hilger, Ltd., 75 A. Camden Road, London, 1921. Price, £1.5s. net.

This book is a compilation of published data on the refractive indices of a very complete list of oils, fats and waxes. The data are arranged in columns, the first of which gives the temperature at which the determination was made; the second, the refractive index; the third, the butyro refractometer reading; and the fourth, the reference number. The arrangement of the figures is good. The oils are placed in alphabetical order. The references appear in the first pages of the book arranged in numerical order. Following this list is an Author index of references, arranged alphabetically, with the reference number included. The list of references forms a good bibliography of the subject of the book.

The compiler says, "It is not the province of a compiler or accept or reject data according to their aspect of verisimilitude to otherwise." It is to be regretted that a sifting could not have been made by so competent an authority, for figures are included which stretch the limits given for certain oils beyond those usually accepted. For instance, in the case of China wood oil there is included a figure considerably below any other quoted, and also below several other figures obtained at the same time on the same oil by other analysts, as shown in the original article.

The temperature coefficients given add to the completeness of the work, and are very useful because they can be employed to shorten the time required to make a determination of the refractive index by permitting the operation to be carried out at room temperature.

In Appendix I the same data as were included for the oils are given for glycerol, for many pure glycerides, and for many fatty acids. In Appendix II are to be found tables showing the refractive properties of several hydrogenated, polymerized or heated and oxidized or blown oils. These data are of greatest value only when all the conditions obtaining during the treatments are given in the tables or in the original article. For instance, the mass of the oil, the material of which the container is made, and its shape influence polymerization reactions. Similarly, the ratio of air volume per unit time to oil volume greatly influences the oxidation reactions when oils are blown. In several instances data of this sort are not available and, therefore, the significance of the figures is reduced.

Appendix III gives the dispersion of many important oils. The reference to the Holley and Brier method for the determination of the purity of China wood oil and the suggestion that the determination could better be made by a direct measurement of the dispersion by an Abbé refractometer is of especial interest to those handling this important oil.

Appendix IV comprises a table of multiples of 0.00037, which is given as the approximate temperature correction for fatty oils to reduce observations to a standard temperature. Appendix V is a table for the conversion of butyro refractometer readings to refractive indices, and vice versa.

Glenn H. Pickard

Cocoa and Chocolate—Their Chemistry and Manufacture. By R. Whymper. xxi + 568 pp. 2nd Edition. P. Blakiston's Son & Co., Philadelphia, 1921. Price, $10.00.

In this second edition the author has more nearly accomplished the object of his first volume, "to provide a standard book of reference dealing with cocoa from its growth till manufactured into cocoa and chocolate," and although perhaps a little disappointing in some respects it is an excellent work on this subject. While written primarily for the chemist and manufacturer, it should also prove of interest to the layman.

The outline of the book is the same as in the preceding volume and contains not only the full text of the first edition, some of which has been revised, but has as much more in addition, with new chapters to include statistics, covering chocolate, nutritive value and digestibility, and the detection of added husks.

The work is distinctly English throughout, and the author repeatedly calls attention to the fact that the American chocolate tastes crude and unfinished and lacks the quality and smoothness of the European product, and although he considers this is undoubtably due to "the prevailing taste which finds the European product slimy and insipid," still feels that too little attention is paid in America to quality manufacture.

The chapter on the characteristics of the various grades of cocoa beans has been entirely revised and is much more in accord with the types of beans as are now found on the market.

In the section on manufacture there is a lack of detail that may prove disappointing to the manufacturer who looks to the book for a variation of his process, for the author finds it difficult to treat this in any but a general manner.

Reference is made in the chapter on "Short Cuts" to "amorphous sugar" which should receive the thoughtful consideration of the manufacturer, for it is in methods of this kind that the expense of producing a fine product can be materially reduced.

The analysis and composition of cocoa and chocolate is treated in the third section of the work in considerable detail, but as would be expected, is of interest mainly to the chemist and leaves a regrettable lack of information on the physical chemistry of the product which is of more far-reaching importance to the manufacturer; for with the exception of the roasting we must deal entirely with the physical changes that take place in the refining, so-called "fatiguing," tempering, and the resulting structure of the finished product. This the reviewer feels, from his own researches on these problems, has not been given the importance it deserves, and must either have not yet been made available, or have been intentionally omitted.

However, there are only too few textbooks on this subject, and this second edition should prove a welcome addition.

Luther Davis

Silica and the Silicates. James A. Audley, B.Sc. (London), F. I. C., Ceramic Chemist. viii + 374 pp. and 27 figures. D. Van Nostrand Co., New York, 1921. Price, $4.50.

This is a volume of the series on Industrial Chemistry prepared under the general editorship of Dr. Samuel Rideal. In his general preface to the series Dr. Rideal proposes a chemical rather than an engineering treatment of the subjects to be included. The latest member of the series is, however, a disappointment in this respect, owing to numerous incorrect and contradictory statements and the general inadequacy of the author's treatment of the chemical aspects of his subject. While it is true that much of the chemistry of this difficult field is at present unknown to us, the extent and exactness of our knowledge is much greater than one would infer from the contents of this volume.

The first few sections of the book give the impression of having been written a number of years ago and published under date of 1921 without revision. Thus we find, in Section I, the dimorphic inversion temperatures of quartz and cristobalite given as 570° and 175°, respectively, while in Section IV the correct values, 575° and 230° to 270°, appear. Again in Section I, we note that "Tridymite is the stable variety of silica above 1500° C. (and near the fusion point)," while in Section IV we are informed that "Tridymite is not known to be formed under any conditions above 1470° C." The entire discussion of the important stability relations of the different forms of silica as presented in Section I is hopelessly incorrect and confused. In Section IV, however, where the author discusses the chemistry of the manufacture of silica brick, these relations are in the main correctly presented and interpreted.

Section II is devoted to the silicates. Here the author adopts a commendably conservative attitude in his brief treatment of the subject of structural formulas. The silicates treated in this section are well selected, and the section, as indeed the whole book, is rich in examples of industrial uses of the various materials. On p. 53 the melting point of calcium ortho-silicate is incorrectly given.

The remaining sections of the book are devoted to lime, mortar, and cement, the "ceramic" (*i. e.*, clay working) industries, glass and enamels, and miscellaneous topics such as alum, soils, and earthy pigments.

For the reader desiring a general survey of the field of ceramic chemistry the book can be recommended and meets a real need. Herein it fulfils its purpose as a member of the series. The noncritical and patch-work character of much of the work, however, renders it of little value to the professional ceramist, for whom it was perhaps not intended. This seems to be borne out by the character of the illustrations, many of which contribute little or nothing to a clearer understanding of the text. The list of references following each section will appeal to those readers desirous of further detailed information.

E. W. Washburn

NEW PUBLICATIONS

American Society for Testing Materials. A. S. T. M. Standards Issued Triennially, 1921. 890 pp. Illustrated. Price, $10.00, cloth; $11.50, half-leather. American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa.

Anthracene and Anthraquinone. E. deBarry Barnett. 447 pp. Price, $6.00. D. Van Nostrand Co., New York.

Cane Sugar, a Textbook on the Agriculture of the Sugar Cane, the Manufacture of Cane Sugar, and the Analysis of Sugar-House Products. Noel Deerr. 2nd edition, revised and enlarged. 650 pp. Illustrated. Price, 42s. net. Norman Rodger, 2 St. Dunstan's Hill, London, England.

Casein, Its Preparation and Technical Utilization. Translated from the German of Robert Scherer. 2nd English edition, revised and enlarged. 216 pp. Illustrated. Price, 11s 3d Scott, Greenwood & Son, London.

Chemical Engineering Catalog 1921. 1294 pp. Price, $10.00 (leasing privilege, $2.00). Chemical Catalog Co., Inc., New York.

Chemical Microscopy: Elementary Chemical Microscopy. Emile Monnin Chamot. 2nd Edition, partly rewritten and enlarged. 479 pp. 162 figures. Price, $4.25 net. John Wiley & Sons, Inc., New York.

Chemical Warfare. Amos A Fries and Clarence J. West. 445 pp. Illustrated. Price, $3.50. McGraw-Hill Book Co., Inc., New York.

Color and Its Applications. M. Luckiesh. 2nd edition, revised and enlarged. 431 pp. 150 illustrations. Price, $4.50. D. Van Nostrand Co., New York.

Food: Probleme und Aufgaben der Nahrungsmittelchemie. Egon Eichwald. 99 pp. Price, $0.75. Theodor Steinkopff, Dresden, Germany.

Handbook: Taschenbuch für die Anorganisch-Chemische Grossindustrie. G. Lunge and E. Berl. 331 pp. Julius Springer, Berlin, Germany.

Iron: Chemical and Metallographic Examination of Iron, Steel, and Brass. William T. Hall and Robert S. Williams. 501 pp. 183 illustrations. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Minerals: Introduction to the Study of Minerals and Rocks. A Combined Textbook and Pocket Manual. Austin Flint Rogers. 2nd edition, completely revised. 527 pp. Illustrated. Price. $4.00. McGraw-Hill Book Co., Inc., New York.

Modern Coking Practice, Including the Analysis of Materials and Products. J. E. Christopher and T. H. Byrom. 3d edition, revised and enlarged. 2 volumes. 280 pp. 145 illustrations. Price, $8.00. D. Van Nostrand Co., New York.

Naval Stores—History, Production, Distribution and Consumption. Thomas Gamble, Editor. 286 pp. Illustrated. Review Publishing and Printing Co., Savannah, Ga.

Oil Trade Calculator. T. Howard Butler. 240 pp. Price, 11s. post free. Scott, Greenwood & Son, London.

Oil: The Fire and Explosion Hazards of Commercial Oils. William Vlachos and C. A. Vlachos. 292 pp. Vlachos & Co., Philadelphia.

Public Health Chemical Analysis. Robert C. Frederick and Aquilla Forster. 313 pp. 60 illustrations. Price, $4.50. D. Van Nostrand Co., New York

Qualitative Analysis: Elementary Qualitative Analysis of the Metals and Acid Radicals. Laboratory Manual. Frederick C. Reeve. 150 pp. Price, $1.50. D. Van Nostrand Co., New York.

Within the Atom: A Popular View of Electrons and Quanta. John Mills. 215 pp. Illustrated. Price, $2.00. D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES

Aluminium Casting. F. A. Livermore. *The Brass World*, Vol. 17 (1921), No. 8, pp. 231–33.

Biochemistry: Modern Views on Biochemistry. W. Gowland Hopkins. *The Chemical Trade Journal and Chemical Engineer*, Vol. 69 (1921), No. 1792, pp. 363–65.

Cements: Plastic Magnesia Cements. P. H. Bates and Roy N. Young. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 7, pp. 570–96.

Chemical Structure and Physiological Action. C. L. Alsberg. *Journal of the Washington Academy of Sciences*, Vol. 11 (1921), No. 14, pp. 321–41

Coal: Recording Ash Pit Losses from Chain Grate Stokers. E. G. Bailey. *The Coal Industry*, Vol. 4 (1921), No. 8, pp. 388–94.

Combustion: Experimental Comparison of a Preheated Air Furnace with a Direct Fired Furnace. O. Lillep. *American Gas Journal*, Vol. 115 (1921), No. 12 (whole No. 3315), pp. 247–52, 260–63.

Dyes: L'Etat Actuel de l'Industrie Mondiale des Matières Colorantes. A. Wahl *Revue Générale des Matières Colorantes, de la Teinture et des Apprêts*, Vol. 25 (1921), No. 296, pp. 113–17.

Dyes: Jute Dyeing. F. C. Holden. *American Dyestuff Reporter*, Vol 9 (1921), No. 14, Sec. 2, pp. 13–14.

Dyestuffs of the Pyrazolone Series. Mary Johnson. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 15, pp. 176*t*–78*t*.

Dyes: Pigment Dyestuffs Derived from Tannic Acid and Some Aromatic Amines. Arthur Ernest Everest and Archibald John Hall *Journal of the Society of Dyers and Colourists*, Vol. 37 (1921), No. 9, pp. 227–29.

Explosives: L'Emploi de l'Oxygéne Liquide comme Explosif Industriel. Charles Lormand. *Chimie et Industrie*, Vol. 6 (1921), No. 2, pp. 141–48.

Fertilizers: Science and the Coming Agriculture. Charles H. MacDowell. *The American Fertilizer*, Vol. 55 (1921), No. 8, pp. 29–33.

Fuel Problem for Oil Shale Retorts. George McD. Johns. *Combustion*, Vol. 5 (1921), No. 3, pp. 121–24.

Gas: Comparison of Efficiency of Industrial Gases. F. J. Denk. *Forging and Heat Treating*, Vol. 7 (1921), No. 8, pp. 422–24; No. 9, pp. 477–79.

Glass: The Composition of Barium Glass. Robert J. Montgomery. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 7, pp. 536–45.

Glass: Free Alkalinity in Glass Containers. A. W. Bitting. *The Glass Industry*, Vol. 2 (1921), No. 10, pp. 235–37.

Glass: The Effect of the Rays from Radium, X-rays and Ultraviolet Rays on Glass. J. R. Clarke. *Journal of the Society of Glass Technology*, Vol. 5 (1921), No. 18, pp. 155–65.

Glass: The Relative Advantages and Disadvantages of Limestone, Burnt Lime, and Slaked Lime as Constituents of Common Glass Batches Containing Soda Ash and Salt Cake. F. W. Hodkin and W. E. S. Turner. *The Glass Industry*, Vol. 2 (1921), No. 10, pp. 237–39; *Journal of the Society of Glass Technology*, Vol. 5 (1921), No. 18.

Glass: Le Soufflage du Verre dans les Laboratoires Scientifiques et Industriels. H. Vigreux. *Chimie et Industrie*, Vol. 6 (1921), No. 2, pp. 160–68.

Heat Balance of a Plant Consisting of an Air-Steam Blown Gas Producer and a Glass Tank Furnace. M. W. Travers. *Journal of the Society of Glass Technology*, Vol. 5 (1921), No. 18, pp. 166–83.

Hydrolysis of Glycerides. *The Chemical Age* (London), Vol. 5 (1921), No. 119, pp. 358–60.

Iron: The Electro-Deposition of Iron. W. E. Hughes. *The Metal Industry*, Vol. 19 (1921), No. 10, pp. 405–07.

Laboratory of the Living Organism. M. O. Forster. *The Chemical Age* (London), Vol. 5 (1921), No. 117, pp. 309–11.

Leather: The Determination of Available Calcium Oxide in Lime Used for Unhairing Hides. F. P. Veitch and T. D. Jarrell. *Journal of the American Leather Chemists Association*, Vol. 16 (1921), No. 8, pp. 438–44.

Leather: Determination of Optimum Temperature and State of Subdivision for Maximum Extraction of Tannin from Goran Bark. B. B. Dhavale and S. R. Das. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 7, pp. 229–39.

Leather: Sampling of Leather and Its Preparation for Analysis—Committee Report, 1921. F. H. Small, Chairman. *Journal of the American Leather Chemists Association*, Vol. 16 (1921), No. 8, pp. 394–430.

National Defense: Les Services Permanents de l'Armeé Scientifique et Technique. I. Les Ingénieurs de la Defense Nationale. Albert Ranc. *L'Industrie Chimique*, Vol. 8 (1921), No. 92, pp. 346–48.

Niter Cake: Methods for the Complete Utilisation of Niter Cake. W. H. H. Norris. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 18, pp. 208*t*–12*t*.

Nitric Acid: The Manufacture of Nitric Acid by the Pot Process. H. W. Webb. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 18, pp. 212*t*–20*t*.

Open-Hearth Furnace Design. A. D. Williams. *The Iron Age*, Vol. 108 (1921), No. 12, pp. 719–21.

Peat: The Uses of Peat in Fuel Manufacture. Hubert Hermanns. *The Coal Industry*, Vol. 4 (1921), No. 9, pp. 439–43.

Rubber: Sull' Azione de Certi Acceleranti della Vulcanizzazione della Gomma Elastica. G. Bruni and E. Romani. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 8, pp. 351–54.

Steel: Carbonizing Manganese Steel. A. A. Blue. *Forging and Heat Treating*, Vol. 7 (1921), No. 8, pp. 413–15.

Straw: The Structure of Cereal Straws. Francis E. Lloyd. *Pulp and Paper Magazine of Canada*, Vol. 19 (1921), No. 37, pp. 953–54; No. 38, pp. 973–76; No. 39, pp. 1002–04; No. 40, pp. 1025–26.

MARKET REPORT—OCTOBER, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Oct. 1	Oct. 15
Acid, Boric, cryst., bbls	lb.	.12$^3/_4$	.12$^3/_4$
Hydrochloric, com'l, 20°	lb.	.01$^1/_2$	.01$^1/_2$
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07	.07
Phosphoric, 50% tech	lb.	.12	.12
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	17.00	17.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb	*.03$^1/_2$	*.03$^1/_2$
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	*.06$^3/_4$	*.07$^1/_2$
Ammonia Water, carboys, 26°	lb.	.08	.08
Arsenic, white	lb.	.06$^1/_2$	06$^1/_2$
Barium Chloride	ton	*45.00	*47.00
Nitrate	lb.	*.08$^1/_4$	*.07$^3/_4$
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works	100 lbs.	2.25	2.25
Borax, cryst., bbls	lb.	.05$^3/_4$	.05$^3/_4$
Bromine, pure	lb.	.20	.20
Calcium Chloride, fused	ton	28.75	28.75
Chalk, precipitated, light	lb.	.03$^1/_2$	.03$^1/_2$
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.00	5.37$^1/_2$
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.50	3.50
Lead Acetate, white crystals	lb.	.12	.12
Nitrate	lb.	.15	.15
Red American	100 lbs.	.08	.08
White American	100 lbs.	.07	.07
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	*1.40	*1.40
Magnesium Carbonate, tech	lb.	.10	.10
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*38.00	*37.00
Phosphorus, yellow	lb.	.30	.30
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.11	.11
Bromide, imported	lb.	*.15	*.14
Carbonate, calc., 80–85%	lb.	.05	.05
Chlorate, cryst	lb.	*.06$^1/_2$	*.06$^1/_2$
Hydroxide, 88–92%	lb.	*.05$^1/_2$	*.05$^1/_2$
Iodide, bulk	lb.	2.60	2.60
Nitrate	lb.	.08	.08
Permanganate, U. S. P.	lb.	*.20	*.18
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.44	.48
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.15	2.15
Caustic, 76%	100 lbs.	4.00	4.00
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.08	.08
Chlorate	lb.	.07$^1/_2$	.07$^1/_2$
Cyanide	lb.	*.25	*.27
Fluoride, technical	lb.	*.10	*.10
Hyposulfite, bbls	100 lbs.	3.50	3.50
Nitrate, 95%	100 lbs.	2.35	2.45
Silicate, 40°	lb.	.01$^1/_2$	.01$^1/_2$
Sulfide	lb.	.06	.06
Bisulfite, powdered	lb.	.06	.06
Strontium Nitrate	lb.	*.12	*.12
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride	lb.	.18	.18
Oxide	lb.	.40	.40
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.09	.09

ORGANIC CHEMICALS

		Oct. 1	Oct. 15
Acetanilide	lb.	*.29	*.29
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.10	.10
Acetylsalicylic	lb.	.56	.56
Benzoic, U. S. P., ex-toluene	lb.	.65	.65
Carbolic, cryst., U. S. P., drs	lb.	.09	.09
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	*.45	*.45
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.15$^1/_2$	.15
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	*.20	*.20
Tartaric, crystals, U. S. P.	lb.	.28	*.28
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12$^1/_2$	.12$^1/_2$
Alcohol, denatured, complete	gal.	.38	.40
Ethyl, 190 proof	gal.	4.75	4.75
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap, refined	lb.	.74	.74
Carbon Bisulfide	lb.	.06$^1/_2$	.06$^1/_2$
Tetrachloride	lb.	.10$^1/_2$	.10$^1/_2$
Chloroform, U. S. P.	lb.	*.38	*.38
Creosote, U. S. P.	lb.	.40	40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.85	2.65
Imported Potato	lb.	.07	.07
Ether, U. S. P., conc., 100 lbs.	lb.	.16	.16
Formaldehyde	lb.	*.11	*.11
Glycerol, dynamite, drums	lb.	.12$^1/_2$	.12$^1/_2$
Methanol, pure, bbls	gal.	1.25	1.25
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	2.08	2.08
Potato, Jap	lb.	.06$^1/_2$	.06$^1/_2$
Rice	lb.	.18	.18
Sago	lb.	.04$^1/_2$	.04$^1/_2$

OILS, WAXES, ETC.

		Oct. 1	Oct. 15
Beeswax, pure, white	lb.	.37	.37
Black Mineral Oil, 29 gravity	gal	.22	.22
Castor Oil, No. 3	lb.	.08$^3/_4$	.10$^1/_2$
Ceresin, yellow	lb.	.08	.08
Corn Oil, crude, tanks, mills	lb.	.07$^1/_4$	.07$^1/_4$
Cottonseed Oil, crude, f. o. b. mill	lb.	.07	.06$^3/_4$
Linseed Oil, raw (car lots)	gal.	.73	.69
Menhaden Oil, crude (southern)	gal.	.35	.33
Neat's-foot Oil, 20°	gal.	1.00	1.00
Paraffin, 128–130 m. p, ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.75	5.75
Rosin Oil, first run	gal.	.35	.35
Shellac, T. N.	lb.	.54	.65
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10$^1/_2$	.10$^1/_2$
Tallow Oil, acidless	gal.	.75	.75
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.77	.75

METALS

		Oct. 1	Oct. 15
Aluminium, No. 1, ingots	lb.	.18	.18
Antimony, ordinary	100 lbs.	4.75	5.00
Bismuth	lb.	1.55	1.55
Copper, electrolytic	lb.	.12$^1/_2$	.13
Lake	lb.	.12$^1/_2$	.13
Lead, N. Y.	lb.	.04$^3/_4$	.04$^3/_4$
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	80.00	82.00
Quicksilver, flask	75 lbs. ea.	*38.00	*37.00
Silver, foreign	oz.	.68	.73
Tin	lb.	.27	.27$^3/_4$
Tungsten Wolframite	per unit	3.25	3.25
Zinc, N. Y.	100 lbs.	4.75	5.00

FERTILIZER MATERIALS

		Oct. 1	Oct. 15
Ammonium Sulfate, export	100 lbs.	2.50	2.75
Blood, dried, f. o. b. N. Y.	unit	4.00	4.00
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	3.00 & .10	3.50 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.85	.75
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American Maker's price).

COAL-TAR CHEMICALS

Crudes

		Oct. 1	Oct. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	.07	.07
Phenol, drums	lb.	.08$^{1}/_{4}$	.08$^{1}/_{2}$
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.45	.45

Intermediates

		Oct. 1	Oct. 15
Acids			
Anthranilic	lb.	1.20	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.50	2.25
H	lb.	1.10	1.10
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.40	2.40
Naphthionic, crude	lb.	.70	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.27	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.18	18
For Red	lb.	.42	.42
Aniline Salt	lb	.26	.26
Anthraquinone	lb.	1.75	1.75
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.50	1.25
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	5.00	5.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.45	.45
Dinitrobenzene	lb.	.25	.23
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.65
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.25	1.25
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.00	2.00
a-Naphthylamine	lb.	.35	.35
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.32	.32
m-Nitroaniline	lb.	.95	.95
p-Nitroaniline	lb.	.80	.80
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	.13	.13
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.85	.85
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.70	1.70
Phthalic Anhydride	lb.	.40	.40
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	1.75	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.42	.40
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.45	.45
o-Toluidine	lb.	.25	.25
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Oct. 1	Oct. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50

Acid Colors *(Concluded)*

		Oct. 1	Oct. 15
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.70	.70

Direct Colors

		Oct. 1	Oct. 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Oct. 1	Oct. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Oct. 1	Oct. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		Oct. 1	Oct. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.75	.75
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Oct. 1	Oct. 15
Auramine, O, domestic	lb.	2.25	2.25
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	2.00	2.00
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	10.00	10.00
Victoria Blue, base, domestic	lb.	5.40	5.40
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

The Journal of

INDUSTRIAL & ENGINEERING CHEMISTRY

Published Monthly by The American Chemical Society

Editor: CHAS. H. HERTY
Assistant Editor: LOIS W. WOODFORD

Advisory Board: H. E. BARNARD J. W. BECKMAN A. D. LITTLE A. V. H. MORY
CHAS. L. REESE GEO. D. ROSENGARTEN T. B. WAGNER

EDITORIAL OFFICES:
One Madison Avenue, Room 343
New York City
TELEPHONE: Gramercy 0613-0614

Cable Address: JIECHEM

ADVERTISING DEPARTMENT:
170 Metropolitan Tower
New York City
TELEPHONE: Gramercy 2145

Volume 13 DECEMBER 1, 1921 No. 12

CONTENTS

EDITORIALS:

A Fireside Chat 1098
CHEMICAL INDUSTRY IN CHINA. William Henry Adolph .. 1099

VITAMINE SYMPOSIUM:

Factors Influencing the Vitamine Content of Foods. R. Adams Dutcher 1102
Standardized Methods for the Study of Vitamines. A. D. Emmett 1104
Vitamines from the Standpoint of Structural Chemistry. R. R. Williams 1107
Vitamines from the Standpoint of Physical Chemistry. Victor K. LaMer 1108
The Antiberiberi Vitamine. Casimir Funk 1110
Experiments on the Isolation of the Antineuritic Vitamine. Atherton Seidell 1111
The Antiscorbutic Vitamine. Alfred F. Hess 1115

ORIGINAL PAPERS:

Some Factors Affecting the Stability and Inversion of Oil-Water Emulsions. Leon W. Parsons and O. G. Wilson, Jr. 1116
The Dehydration of Tar in the Laboratory. Wilbert J. Huff 1123
Benzenedisulfonic Acid from Benzenemonosulfonic Acid. C. E. Senseman 1124
The Electrical Conductivity of Solutions of Zinc Sulfate in the Presence of Sulfuric Acid. Herman V. Tartar and Harmon E. Keyes 1127
Recent Development in the Art of Rubber Microsectioning. Henry Green 1130
The Relation between Coefficient of Vulcanization and Mechanical Properties of Vulcanized Rubber. O. de Vries 1133
The Properties and Action of Enzymes in Relation to Leather Manufacture. Joseph Turney Wood ... 1135
A Critical Study of Bating. John Arthur Wilson and Guido Daub 1137
Cider Preservatives. R. D. Scott and E. G. Will 1141
A New Qualitative Test for Sucrose in the Presence of Glucose. Leon A. Congdon and Charles R. Stewart 1143
Potash Shales of Illinois. M. M. Austin with S. W. Parr 1144
The Determination of "Strength" or Neutralizing Power of Acid Calcium Phosphates. W. E. Wadman 1146
The Determination of Moisture in Insulating Oils. C. J. Rodman 1149
Method for the Determination of Free and Combined Carbon Dioxide. J. A. Shaw 1151
The Effect of the Presence of Filter Paper on Permanganate-Oxalate Titrations. Stephen G. Simpson 1152
The Formation of Oxides of Nitrogen in the Slow Combustion and Explosion Methods in Gas Analyses. G. W. Jones and W. L. Parker 1154

LABORATORY AND PLANT:

Revised Specific Gravity Table for Orthophosphoric Acid at 25°/25° C. N. P. Knowlton and H. C. Mounce 1157
Graded Seal for Joining Pyrex to Lead Glass. W. C. Taylor and Austin Bailey 1158
SPECIAL COST FACTORS AND THEIR RELATION TO THE DEVELOPMENT OF OUR ORGANIC CHEMICAL INDUSTRY. Gaston Du Bois 1159

SOCIAL INDUSTRIAL RELATIONS:

Food and Shelter. H. W. Jordan 1161

NOTES AND CORRESPONDENCE:

A Study of the Fundamental Laws of Filtration Using Plant-Scale Equipment; The Variability of Crude Rubber; The Nitrogen Supply of the World; Adoption by the Colleges of Standard Metric Unit—Addendum 1163

SCIENTIFIC SOCIETIES:

Synthetic Organic Chemical Manufacturers Association of the United States; The 1921 Meeting of the Association of Official Agricultural Chemists; Calendar of Meetings; Cornerstone Laid for New Cornell Chemical Laboratory; Local Section Meetings; Honorary Members of the American Chemical Society; An Englishman's Impressions of the New York Meeting; Plant Excursions, New York Meeting; Chemistry and Disarmament 1168

MISCELLANEOUS:

American Association of Textile Chemists and Colorists 1162
American Field Service Fellowships for French Universities 1126
Perkin Medal Award 1126
Plan Campaign for Standardization of Biological Stains 1158

WASHINGTON LETTER 1171
PARIS LETTER 1172
INDUSTRIAL NOTES 1173
PERSONAL NOTES 1173
GOVERNMENT PUBLICATIONS 1174
BOOK REVIEWS 1176
NEW PUBLICATIONS 1178
MARKET REPORT 1179
AUTHOR INDEX 1181
SUBJECT INDEX 1187

Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage, 75 cents, Canada, Cuba and Mexico excepted.
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G Street, N. W., Washington, D. C.
Member of Audit Bureau of Circulations

EDITORIALS

A Fireside Chat

A friend in a somewhat philosophic mood recently remarked, "Some day when we are old men sitting before a memory-stirring fire on a winter's evening, we are going to look back upon this five-year period in American chemistry, and it will seem like a romance, with its recollections of intense efforts and speedy accomplishments, and its thrill of patriotic service." We agreed, of course. But while preparing to leave the old chair where five happy years have been spent we glanced over the scrap book containing the editorials from This Journal. These stirred our memory, and brought forth the conviction that it will not be necessary to wait until we are old men to get this sense of romance, this thrill of things accomplished. Draw your chairs up before the fire, the gas log, or the radiator, wherever in this broad land of ours you may be meeting the chill of this first touch of winter, and let's talk it over.

The story began in 1916 when consumers were suddenly faced with a cessation of imports of dyes. Do you remember the cry that went up from certain quarters, blaming the American chemist for not having a dye industry ready to meet the shortage, as if such a thing were kept in the ice box ready to serve when the cook is suddenly taken ill? Then, when an effort was made to begin manufacture of dyes and to secure protective legislation for the industry, propaganda, a word seldom heard at that time, showed its head in the shape of that industriously circulated but weird myth that dyes couldn't be made from American coal. That bird was soon shooed off that perch, only to light on the declared inability of the American chemist to make dyes. Again the bird has been dislodged.

Mr. Kitchin emasculated the legislation intended to safeguard the industry, but we believe Mr. Kitchin eventually regretted this, when he learned that Hugo Schweitzer wrote in detail to von Bernstorff how this impotent legislation guaranteed the eventual death of the American industry and recovery of the market by the German industry.

Nevertheless the industry has grown, filling more and more America's needs. With the development of gas as a means of warfare the industry has taken on a new and significant aspect. For this reason its safeguarding has been urged by former President Wilson, and more recently by General Pershing, Secretary Weeks, Secretary Denby, Secretary Hoover, Brigadier-General Fries, and Rear-Admiral Strouther Smith.

Let's go back again, now, to the time when the War Department, months after we had entered the war, felt that chemistry had no special part to play in warfare. Don't you remember the long up-hill fight that was required to keep the chemists from the Front, to avoid the very mistake that France and England avowedly so bitterly regretted? A whole year was required to force the conviction of the necessity of organizing chemists in a special branch of the Army. But the conviction finally came, and then was organized one of the most capable units in the world, the Chemical Warfare Service.

With the war over, retrogression immediately began; the Chemical Warfare Service was precipitously demobilized and the then Secretary of War and Chief of Staff got out their knives for the C. W. S. in the Army Reorganization Bill. Another fight was required and eventually won, when the Service was made a separate unit of the Army.

Read again the editorial, "Toluol, Toluol, and Then Toluol." Strange that, knowing full well the importance of TNT, and planning to raise an army of millions, we continued to burn the crude throughout the length of the land. Soon, however, the situation was completely changed.

Don't you remember the days when chemists were urging the conservation of platinum for government munition plants, and how the jewelers did oppose the effort? It was very thin ice on which the War Industries Board was skating, so far as platinum was concerned, toward the close of the war. There is still a remarkable story connected with this platinum campaign which some day may yet be told.

Perhaps one of the most far-reaching actions of this war period was the inauguration of lectures at West Point and Annapolis by distinguished members of the AMERICAN CHEMICAL SOCIETY. As the years go by the good effects of these lectures will make themselves felt more and more. We would prefer talking about the hopes of all of us for a successful outcome of the Conference on Limitation of Armament, now sitting, but so long as we must have any army or navy, these should be officered by men who understand the fundamental importance of chemistry in war making.

What about duty-free importation of scientific apparatus, glassware, and other tools used by the chemist? This is a subject that fascinates us from two points of view. First, confidence and inspiration are gained when it is remembered how quickly technical problems have been solved, thereby making available wares of the highest class of manufacture. Second, loyalty and foresightedness have been demonstrated in the way chemists have stood by the home manufacturer in spite of the allurements of duty-free importation privilege and depreciated foreign exchange.

Someone asks, "What has become of the Institute for Chemo-Medical Research?" Was the tone indicative of a belief that this movement has been forgotten? If so, you've missed your guess, old man. True, the Institute has not yet materialized, but we venture a prophecy—some day it will be an actuality! This confidence is based upon knowledge of the thorough report which has been prepared by the Committee at the request of the Chemical Foundation. It is now in the hands of the printer, and will be given wide distribution by the Foundation.

Let's not break up this chat without a few words about the chemist who is waking up to his responsibilities of letting his fellowman know something about what he is doing and how closely his work touches every phase and activity of life. That is the real miracle of the past five years. In accomplishing it there have been utilized the daily press, the magazines, popular books on chemistry, the Chemical Exposition, public addresses, and personal conversations. The response of the public has been fine and America is better off to-day because of it all—and that is the main point.

Now it's time to break up. The predetermined limits of space for this final chat tell us that closing time has come. We are not going to say good-by, for we are not going away, only going to work in another room of this house of our national welfare, a room into which many of you will some day enter. Here's hoping we may be able to be of some service in making that next room a place where you can show forth the best talent of the American chemist. It has been a great joy to work with you during these five eventful years. It will be a happiness to work for you during the years to come. And it is fine to know that during those coming years This Journal will be in the hands of one whose talents so fully qualify him for the work and whose devotion to the AMERICAN CHEMICAL SOCIETY is second to none. Here's Howe!

CHEMICAL INDUSTRY IN CHINA[1]

By William Henry Adolph

Shantung University, Tsinan, China

Rapid growth and changes in chemical industry in the United States in the last few years have been paralleled by developments of a similar magnitude in China and the other countries of the Orient which were only indirectly touched by the world war. The entire country has reacted rapidly to a number of stimuli, and has presented on the one hand a phenomenal growth in existing industries, and on the other hand a revelation of still more striking latent industrial possibilities. These stimuli have been partly the competition aroused by the aggression of other nationals in the country, and partly of a political nature connected with the prominence given the Shantung question at the peace conference.

Economic engineers have for some time projected industrial enterprise as a solution to relieve the effects of the tremendous population pressure in China. China has been essentially an agricultural country. The last two or three years have seen an enormous step in the direction of her industrial independence. The mysterious Orient is a thing of the past. During the space of a five years' residence in Shantung, the writer has made a number of notes which a certain professional duty seems to suggest should be passed on.

The developments in Shantung are typical of China as a whole. Shantung silk and peanuts have already immortalized the province. The Shantung silk, called *pongee* on the market, owes its peculiar qualities to the fact that the silk worms are fed on oak leaves, not on mulberry. Shantung hides and oils are rapidly coming to the fore. The causes which have held back these and other industries are twofold: one, a certain lack of trained technical experience on the part of the Chinese operators; the other, the failure on the part of foreign manufacturers of machinery—this trait is largely true of Americans—to study sympathetically the peculiar needs of the Chinese industry, and to design and adapt plant and machinery to the requirements of a less completely organized industry. America, not Japan, strangely enough, has replaced Germany in the affections of the Chinese industrialist. But we in the United States have not risen to our opportunity.

America may well take a lesson from Germany's methods in stimulating chemical industry in Shantung. Her expert studied the industrial needs of the province, designed machinery and plant of a type which was not used in Germany but which was needed in China. Our America houses too often have sent their catalogs and given up in despair when an order was not received by return mail. But the Germans cultivated the market, then patiently waited, taught, established industrial schools, were patient again, and built themselves into the good graces of the people. Even now the field is still a virgin field, and it requires expensive and rather tender cultivation on the part of the industrialist and commercial man. An enterprising peanut-oil producer knows perhaps how to run an oil press, but is unable often without help to order the machine he needs from the confusing specifications of an American catalog, and to instal it.

Americans traveling in China are astonished at the extent to which intelligent Chinese are looking to America as the source of new inspiration and help. In traveling through China, the writer found the simple statement that he was an American the most powerful password that could have been given. He was still more interested in observing the care with which his Chinese associate on industrial trips mentioned that the foreign visitor was an American. It invariably meant the doors were thrown open with a willingness. This was in spite of the fact that the Chinese manufacturer has preserved a good bit of his medieval reticence, and is cautious about imparting family trade secrets.

The situation in China divides itself into the recognition of two kinds of industries, with two kinds of industrial problems. In the first place are the old Chinese chemical industries, dyeing, glass, paper, etc., which had their origin in China's prehistoric days. In the second place are the chemical industries which are new to China, sulfuric acid, soda, tanning, which are now looked upon as the foundation stones of a modern chemical industry. It is these which have now to be founded from the very beginning.

The first, the old industries, will help fill some of the pages of our history of chemical industry, and will furnish some of the curious illustrations of how practice can race away from theory till theory is lost thousands of years behind. In China these were all small-scale industries, many of them family industries, and in most cases only supplementary to various phases of agriculture. They require a development that will enable them to retain their important position in the economic fabric of the country, and at the same time to satisfy the requirements of modern efficiency. The second, the new industries, involve serious financial problems as well as technical ones.

The Made-in-China Movement

The "made-in-China" cry which accompanied the recent patriotic movement has taken a real place in the life of the country, and it has not turned out to be but a fleeting enthusiasm. High-school graduates, and ex-soldiers whose experience has been limited to the manufacture of soda-water and vending of opium pills, have set up as chemical manufacturers, and the desire to *make*, instead of *import*, will gradually affect the status of our commercial relationship with China.

News came to us recently of a newly founded sulfuric acid plant in central Shantung, where pyrite was plentiful and fuel cheap; they were reported to be in difficulty. On arrival, our surprise was exceeded only by a certain amount of pathetic admiration. A couple of thousand dollars, all the money the investors possessed, had been expended in the erection of a small plant for the manufacture of sulfuric acid by the chamber process. There were four little lead chambers in a row, a pyrite burner was located at one end and at the other end was an outlet pipe for the excess gases. The manager, who was a high-school graduate and had studied a half year of chemistry in high school, stepped proudly forward, and explained that he had designed the plant unaided and that the completed plant was an exact copy of the diagrammatic sketch which was to be found in his high-school textbook. The plant had failed to produce satisfactory acid. The "company" was profoundly disappointed when shown that there were a number of important details which had been omitted in the crude sketch. This is not an isolated case of patriotic enthusiasm.

The "made-in-China" movement also manifested itself in other ways. A short time ago there was erected a high and imposing chimney, with the elements of a factory attached to its base. In a few days the chimney started

---

[1] Received September 6, 1921.

spurting heavy nitric fumes, and simultaneously with the appearance of the fumes there were scattered broadcast over the Chinese republic handbills announcing the founding of a Chinese company for the manufacture of synthetic dyes in China to replace the imported variety. Patriotic Chinese dyers responded with enthusiasm; the new made-in-China dyes prospered with alacrity. The factory became the center of some interest, but visitors were not encouraged. An investigation showed that there were two doors in the factory. Into the east door were hauled on high single-wheeled barrows cases of imported dyestuffs. On the trip through the factory, the cases were opened, labels removed and changed for made-in-China labels, and the dyes were wheeled out the west door to parade as Chinese product. The yellow smudge which appeared from the stack was kept going constantly while the process of pasting on new labels proceeded.

Resume of Chemical Industries

It is possible to make only a partial list of the principal industrial items which are of interest to the chemist in China.

ALCOHOL—Very little industrial alcohol is manufactured in China. Alcoholic beverages have been used and prepared by the Chinese for ages. There is, however, a large variety of cheap materials aside from grains and sugar wastes which can be used in an alcohol industry.

BLEACH AND BLEACHING—A growing textile industry is demanding large quantities of bleaching powder and other chemicals which have not been used in the past. The new hair-net industry sends hundreds of pounds of old queues, cut off under the republican régime, to the United States to be bleached and dyed, and then has them shipped back to China for making into hair nets for the American market. The desire on the part of China to compete with foreign manufactured articles of all kinds calls for bleaching of the raw materials. The proper conditions exist for the establishment of an electrolytic bleach industry. No electrolytic industrial processes have yet been founded in China.

CEMENT—A few cement mills have been erected to take advantage of excellent raw materials. The Chinese sources of supply do not, however, fill the increasing demand for this and other building materials. Boshan, the ancient glass center in Shantung, is one of the centers where the cement industry would naturally be developed. The writer has examined many old structures and ruins of masonry which indicate that excellent concrete was used by the Chinese from very ancient times.

CHEMICAL FERTILIZERS—China is an agricultural country and several thousand years of intensive cultivation have exhausted the soil. Crops are raised only by the regular application of fertilizer. This consists principally of sewage, which is dried and marketed; its preparation forms the foundation of a widespread industry. In the absence of any sewer systems, it has been possible to make almost full return of the nitrogen to the soil. The rapid application of scientific methods to agriculture as well as modern principles of sanitation is beginning to demand the building up of a chemical fertilizer industry.

CHEMICALS. *Acids*—Pyrite is found in fair abundance in China, but sufficient capital and protection have not yet been united to insure a sound sulfuric acid industry. One large acid works has been in operation successfully for a number of years, and a number of others have been planned. No attempt as yet has been made to manufacture C. P. acids. The lead-chamber process is employed in all cases. Nitric acid is manufactured on a small scale.

Alkalies and Soda—Native soda and potash exist in China, but are failing to meet the heavier demands of modern industry. A number of LeBlanc soda works are being erected and conducted under the guidance of American trained experts.

Saltpeter—In a country so densely populated as China the accumulations of waste nitrogen in densely inhabited centers is considerable. A quantity of saltpeter is produced annually by scraping off the top surface of the ground in and around the dwellings and stables where this can be done conveniently, particularly in the country districts. The material is treated with wood ashes and extracted, and the potassium nitrate is allowed to crystallize.

Alum, Borax, Glauber's Salt, Green Vitriol, Copperas—A number of these fundamental chemical compounds are found native in China or have been manufactured by crude methods since ancient times.

DYES AND DYEING—China possesses and has used for centuries a large group of vegetable dyes, among them indigo, saffron, and a number of yellows, browns, and blacks. These the Chinese have used only in a very crude way, and some of them have been only partly studied, if at all. The fact that the Chinese have not developed their native dyes in a scientific manner is largely responsible for the present large demand for synthetic dyes from abroad.

Synthetic indigo had efficiently stamped out the native indigo which history indicates had its origin in Shantung, China, many centuries ago. The war revived the industry, which is strong in the north. It remains to be seen how the growing of native indigo, which has been on the increase, will survive under modern scientific management. German trade had done much to kill all of China's native dyes, but the war forced a certain return to the use of native dyes and to a certain extent forced the beginning of a scientific investigation of China's natural wealth in dyestuffs.

EGGS, DRIED ALBUMEN, DRIED EGGS—Chinese eggs are much smaller than American eggs and for that reason, in spite of their cheapness, they have not met with favor as fresh eggs on the American market. The price of eggs in China has risen considerably during the last decade, till they now cost about 5 or 6 cents (U. S. currency) per dozen in the egg-producing districts. The dried egg industry has flourished in China for about ten years. The egg is dried in zinc pans whole, or the yolk and albumen may be dried separately. The U. S. Customs requirement, dating from a few years ago, that the zinc content must be less than 0.1 per cent, almost killed the industry, but it recovered with the introduction of the newer method of spray drying. The lay of Chinese hens in Shantung province is higher than the remainder of China, said to be due to the fact that Shantung chickens are fed soy beans, which contain a high percentage of protein. An opportunity exists for the use in China of this large supply of cheap albumen. Attempts have been made to develop the manufacture of artificial ivory, and similar products.

GLASS—Glass has been manufactured in China from prehistoric times, and in the two or three centers where it has been carried on essentially the same methods as were employed in ancient days are now used. Window glass is also manufactured, and improvements are gradually being introduced. One of the first constructive steps furthered by the Germans in Shantung was the establishment of a large glass works. They employed a large staff of Belgian experts to train the Chinese workmen. This particular works was closed in 1914.

MATCHES—The Chinese were quick to see the advantage of matches over flint and steel, and one of the first of the smaller modern industries to flourish was the manufacture of matches. The white phosphorus and other chemicals required are imported, and sometimes the wooden sticks and boxes also, the only cheap materials being the labor involved. The imported phosphorus is in turn derived from bones originally exported from China.

METALS AND MINERALS—It was the reports of China's fabulous mineral wealth which first drew the attention of the Occident, and it is the mining industry which is seeing the gradual disappearance of traditional unscientific methods. The old method of developing mines in China is well illustrated by the story of the founding of the Hanyang Iron Works. The machinery and equipment for this were ordered by an enterprising old viceroy, who knew neither where he was going to locate the plant nor the kind of ore it was to handle, for the ore had not yet been discovered. When he ordered the outfit he was stationed in Canton, in south China; when the machinery arrived, he had been transferred to central China. It was a piece of remarkable good fortune that ore suitable for the type of plant which he had ordered was soon found at his new post, Hankow, and that a coal mine to furnish fuel for running the plant was found nearby.

The mining industry of China for many years was largely a contest between enterprise and the desire of officialdom to share in the profits. Actual prejudice and superstition were not such important factors as often imagined; but successful mining has depended upon the clever manipulation of legal as well as other kinds of machinery.

All the common metals and minerals are found in China, with the exception of any appreciable quantities of gold or petroleum. The mineral wealth of Shantung was largely responsible for Germany's decision to make that her sphere of influence. Those which have drawn considerable attention during recent years are:

Coal—The coal reserves of China half a century ago were estimated to be limitless. Saner surveys now place the figure at about the same as that for the United States; moreover the coal is found in every province, not simply in favored areas. The annual output is at present about one-thirtieth of that in this country. Shantung province does not possess as much coal as it did in Germany's dreams. There are very large deposits of anthracite in China as well as all other varieties. China has just entered upon the role of coal exporter to Europe. The production for 1920 totaled 13,000,000 tons, of which over one-half was anthracite.

Iron—The glowing reports of von Richthofen, Germany's early scientific emissary to China, which told of unlimited reserves of iron ore have also been shown by careful studies to be erroneous. The present estimates place the workable iron reserves at 400,000,000 tons. The production of iron per capita in China is only one-three hundredth of that in the United States.

Antimony and Tungsten—China furnished the world with antimony and the production was stimulated tremendously by the war. Tungsten ore was likewise developed, but the rise in exchange and the attempt of official interests to tax the profits killed this industry and seriously crippled the antimony trade.

PAPER—Hand-made paper has been in use for centuries. The paper, however, is of inferior grade, and does not seem to have shown any improvement during the course of the centuries. Only one modern paper-mill complete with calender machines exists, and this uses old rags as the sole raw material, of which there is an abundant supply in China. The product of this mill has difficulty in competing with imported paper, but the difficulty probably lies, like many other Chinese industrial difficulties, in inefficient management. The future of the paper industry seems to depend upon the discovery of a new Chinese raw material. This is bound up with the fuel question, for all grass and weeds are at present used for domestic fuel and heating; wood, except the bamboos of the south, is too expensive or nonexistent.

POTTERY—China has excelled in the production of glazed ware and porcelain, but the industry still remains on much the same basis on which it has rested for many centuries. The country possesses excellent raw materials, and a number of recent attempts have been made to produce fine heat-resistant porcelain for modern laboratory use, but without marked success.

SALT—The production of salt has long been a government monopoly, and the salt tax is one of the government's principal sources of income. The high duty has hindered the development of industries using salt as a raw material. Salt is mined, and brine, both from wells and sea water, is evaporated by solar evaporation. The ancient salt wells of western China, many of them 2500 to 2800 feet deep, are one of the industrial curiosities of the Far East. Use is even made of the salt bittern or mother liquor, which is sold for use as a coagulant in the manufacture of vegetable cheese.

SOAP—In many places in interior China, the Chinese have used varieties of vegetable soap. This is derived usually from a soap bean and contains principles identical with or similar to saponin. The manufacture of soap sprang up all over China with the introduction of the principles of modern chemical industry, and American and European imported soaps are now meeting serious competition. Crude methods are in many places still employed and the products placed on the market are often of doubtful value. There is need for an experienced and well-trained personnel in developing this industry.

SOY BEANS—The soy bean of north China not only is the source of the bean oil which is now the leading article of China's exports, but is the source of numerous other products. The press cake is being used for fertilizer on the rice fields of Japan and seems to meet a special need there which cannot easily be replaced by other varieties of fertilizer. The only serious question to China is that it means the annual shipping out of the country of large amounts of protein material which China should have for use at home. A movement is on foot to make use of the casein which can be prepared from the soy bean and to turn it into a product like the American bakelite.

SUGAR—The cane-sugar industry has been long established in south China, and the beet-sugar industry has just recently been established in Manchuria and Shantung. Considerable progress remains to be made in the methods for refining the finished product.

TANNING—Cattle raising and the production of hides is a growing industry in north China and Mongolia. The old method for curing leather was not tanning at all. The word "American leather" during the last decade had come to be synonymous with the word for good leather, and the new move to establish home industries included the demand that China's hides must be tanned at home. This is far from being accomplished, but rapid progress is being made. Chrome leather is now produced successfully, and the other processes are gradually being put into operation. The need is for trained and experienced leather men.

VEGETABLE OILS—The oil industry in China includes: castor oil, cottonseed oil, peanut oil, sesamum oil, soy-bean oil, tung oil (China wood oil). These oils have long been produced and fill certain domestic needs. The progress of the last few years has meant little else than the extensive substitution of modern machine presses for the old-time crude and clumsy wedge devices for squeezing the seeds till a fair amount of the oil was expressed out. Practically no study has been made in China of the refining and proper standardization of these oils for the industries. Many of the oils will ultimately be worked up into their various products with profit before being exported. No paint industry has yet been developed. All good paint is imported, though all the necessary raw materials exist in the country for a prosperous industry. The Chinese have been satisfied in the past with a few kinds of good but extremely expensive lacquer, and with poor types of varnishes and paints made from oils which at best were only semi-drying oils. The improvement of the tung-oil industry starts with the growth, selection, and improvement of the tung tree.

Conclusion

The writer is anxious to urge that the chemical industries of China need our sympathetic interest in their development, and also a goodly amount of American capital. The industrial situation is characterized by cheap labor, and by a surprising manual skill and power of application on the part of the Chinese workman.

This open door is an industrial one; it is not merely a political phrase. In spite of ourselves, American interests are being dragged into the China field. American locomotives in increasing numbers are appearing on the Chinese railways. It is significant that not we, but our American-trained Chinese students, are putting them there.

One is impressed by the fact that the discussions of industrial problems which appear in the journals of this country are so easily limited to the boundaries of the United States; on very special occasions they may be extended as far as Alaska or the Philippines. Astounding revelations of the ignorance of technical men in the United States upon the needs and problems of the industrial world abroad crop up. A few years ago an American consulting engineer who pretended to cater to the oriental field and who was anxious to keep us in China supplied with all the catalogs and literature on the latest types of machinery, sent a supply of pamphlets expounding the virtues of a new device which was just appearing on the market—a stump-puller. His machine might have been used in clearing the primeval forests of central Africa, but Shantung had been for so many treeless centuries in the grip of floods and famines, with mountains bare and every inch of soil under such intensive cultivation, that we could have desired nothing so much as a single stump to pull. There are frequent evidences of our lack of information on the geography of the districts abroad which we plan to serve in a technical capacity.

VITAMINE SYMPOSIUM

Papers presented before the Division of Biological Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

Factors Influencing the Vitamine Content of Foods

By R. Adams Dutcher

Department of Agricultural Chemistry, Pennsylvania State College, State College, Pa.

Probably no phase of the vitamine question is attracting greater attention at the present time than that which has to do with the vitamine content of our natural and prepared foods and feeding materials. Hardly a week passes that the writer does not receive letters from teachers, housewives, dairy-men, and manufacturers, asking for advice regarding the effect of this or that process of food treatment upon the vitamine content of the particular article of diet in which they are interested. It is difficult, if not impossible, to answer many of these questions satisfactorily for the reason that many of the problems have not been investigated and many of those which have received attention have been influenced by so many factors that it is difficult to say with any degree of certainty what the real facts may be.

In a paper of this type it is impossible to do more than point out what seem to the writer to be some of the outstanding phases and to emphasize some of those factors which seem to be of the greatest importance.

Foods of Plant Origin

It is quite clear that fresh undried cereals possess antineuritic and antiscorbutic properties that are not manifest in the dried seed. While the antineuritic vitamine occurs more or less abundantly in the dried cereals, it is found that the antiscorbutic vitamine has practically disappeared during the drying process.

When seeds are allowed to germinate,[1,*] however, it is found that they possess marked antiscorbutic potency and their value with regard to the antineuritic vitamine has been enhanced to some extent. The British military authorities[2] have made use of this fact by requiring the use of sprouted beans as an antiscorbutic food for certain of their expeditionary forces.

Steenbock[3] argues that most plant tissues, which are characterized by the production of carotinoid pigments, are relatively rich in the fat-soluble vitamine. He is of the opinion that these pigments are very closely related to the fat-soluble vitamine or are identical with it. Palmer,[4] Drummond and Coward,[5] and Stephenson[6] do not hold this view and cite experimental evidence to disprove Steenbock's generalization.

The relationship between metabolic processes in the plant and the production of fat-soluble vitamine is not at all clear, and the fact that plant leaves are rich in this accessory factor has caused considerable speculation. Some writers maintain that the vitamine is a result of or associated with metabolic processes. This is supported by the fact that the vitamine content of plants such as the carrot[7] and alfalfa[8] seems to be at its maximum during the early stages of growth, when the plants are young and when metabolic processes are most active.

It must be of considerable satisfaction to the botanist to know that the animal kingdom is dependent upon the plant world for vitamines as well as the other nutrient materials. It appears to be quite evident that the animal body cannot synthesize vitamines, at least to an extent where they can be considered of dietary importance.

Foods of Animal Origin

There are undoubtedly four factors operating to influence the vitamine content of fleshy foods: (*a*) The diet of the animal previous to slaughtering, (*b*) the type or species of animal, (*c*) the type of tissue used as food, and (*d*) the method of food treatment.

With reference to the first factor, *i. e.*, the diet of the animal, the evidence points to the fact that the vitamine content of body tissues must, of necessity, be influenced by the vitamine content of the diet. Drummond and his coworkers[9] have shown that lard does not usually contain the fat-soluble vitamine, owing to the fact that the ration of the

---

[*] Numbers in text refer to Bibliography, p. 1104.

hog is invariably deficient in this particular food factor. This is a partial explanation for the differences in the body oils of different types of animals. That the vital organs of the type represented by the liver and the kidney are rich in vitamines A and B scarcely needs comment. Food treatment will be discussed later in this paper.

When we consider dairy products we are confronted with a similar situation. While milk is undoubtedly one of our very valuable foods in this regard, it is possible to produce milk which is almost devoid of vitamines. At its best, milk cannot be considered an antiscorbutic food unless it is consumed in quantity.

In our work at Minnesota,[10] we have shown that milk may be relatively rich or very poor in antiscorbutic potency, depending upon the vitamine content of the cow's ration. Our work indicates, also, that the antiscorbutic properties of milk are most easily affected by feeding, although Dr. Kennedy has collected data which show that the fat-soluble factor is also susceptible of considerable fluctuations, which appear to be seasonal in ordinary dairy milk. We are now preparing data, for publication, which show that rats will grow normally when the fat-soluble vitamine is furnished by a ration containing 5 per cent of butter obtained under ideal feeding conditions. On the other hand, we have been unable to obtain normal growth when this vitamine is furnished by a ration containing 20 per cent of butter fat produced on a vitamine-poor ration. We have found, also, that 10 cc. of milk, produced on vitamine-rich rations, will usually furnish sufficient vitamine A and vitamine B for normal growth, while larger quantities of milk, produced on vitamine-poor rations, were very deficient in both of these food accessories.

In addition to seasonal variations in the vitamine content of milk, we have observed marked effects of climatic conditions. Periods of drouth, followed by browning of the pastures and drying of the grass, are reflected in the growth curves of the experimental animals. These results are in agreement with those which were obtained in a similar study on the antiscorbutic vitamine. Other investigators have reported similar observations.[11] It is quite evident that the water-soluble (B) vitamine does not fluctuate to any considerable extent, on account of the fact that most dairy animals receive some grain. This is not true for all dairy stock, however, for the writer has seen cattle go through the winter on some western farms on a diet composed very largely of straw. There is little wonder in such cases that the animals have a rough, unthrifty appearance by the time the spring months arrive. Certainly the milk and butter from such animals must be almost devoid of vitamines. It may be said, for the benefit of Dr. Steenbock, that our vitamine-poor butter was practically colorless. These observations on the influence of diet are of far-reaching significance, not only in commercial dairy production but with reference to the intelligent feeding of all lactating animals. Furthermore, intelligent feeding in the dairy industry means not only higher production but more nutritious milk and butter.

No systematic investigations have been made relative to determining the best winter feeds to employ for the production of vitamine-rich milk. Silage does not appear to enrich milk as far as the antiscorbutic vitamine is concerned. We have observed that good, green alfalfa seems to improve the nutritive value of the milk, but in just what way we are not prepared to say. There is every reason to believe that the nutritive value of eggs may be influenced by feeding. The practice of feeding sprouted grains to poultry during the winter months should produce eggs containing increased amounts of both the fat-soluble and water-soluble (B) vitamines.

The Influence of Food Treatment

Very little has been published concerning the influence of chemical environment upon the stability of the vitamines A and B. It is apparent that the antiscorbutic vitamine is fairly stable in an acid environment,[12] while it appears to be less stable to alkalies.

As a rule foods seem to lose their vitaminic activity during long periods of storage. Just what factors are operating under such conditions, it is difficult to say. Certainly oxidation must be considered.

Many desiccated foods appear to have lost their activity during the drying process, while others have not. There are several factors to be considered in this regard. First of all, not all investigators work with the same quantities of material in their feeding trials. In the second place, the original vitamine content of the desiccated food must be taken into consideration. Unless such materials are fed at the lowest level, in the fresh condition, it is conceivable that, although vitamine destruction takes place, there may be a sufficient quantity remaining to supply the experimental animals adequately. Discrepancies in the literature may be explained, quite often, on this basis.

Often temperature studies cannot be depended upon owing to the fact that oxidation factors have been ignored. Hopkins,[13] Hess,[14] Zilva,[15] Drummond and co-workers,[16] and others have shown that the fat-soluble and antiscorbutic properties of foods are destroyed by oxidation. Our own work supports this. Edla Anderson, working in the writer's laboratory, has shown that oxidation destroys the antiscorbutic value of milk, while pasteurization in closed vessels or boiling does not affect the milk appreciably. Her results indicate, also, that high temperatures for a short time are less destructive than lower temperatures for longer periods. Harshaw and Hall, also working in the writer's laboratory, have shown that orange juice loses its potency in the presence of hydrogen peroxide, even at room temperature. Boiling, however, in the absence of hydrogen peroxide does not appear to have a harmful effect. Heating in the presence of hydrogen peroxide hastens the oxidative destruction.

Mr. Ackerson, one of the author's students, constructed a milk-drying apparatus in which milk was dried in an excess of hot air. The milk particles during the drying were not subjected to a temperature exceeding 110° C. The temperature of the box did not exceed 120° C. This milk powder was valueless as an antiscorbutic food, although the same quantity of raw milk possessed some antiscorbutic potency. No detailed studies, so far as the writer is aware, have been made in this regard, on the effect of drying and curing of hay and, for that matter, many human foods.

A prominent dairy authority informs the author that his observations have led him to the belief that there is considerable fluctuation in the nutritive values of hays grown on the same land from season to season. He is of the belief that the conditions of drying and curing are very largely responsible for these differences, although the maturity of the plant at the time of cutting must be considered. Practical feeders have observed that bright green alfalfa, properly dried and cured, is superior to the light colored crops, bleached out by unsatisfactory climatic conditions or careless agricultural practice. Careful investigation of the vitamine content of the leafy hays produced under various conditions of drying and curing should yield information of scientific and practical importance.

No comprehensive work has been done upon the changes in the vitamine content of silages of various kinds in comparison to the vitamine content of the fresh agricultural plants from which the silages are made. This information is badly needed in order that the winter ration may be of the highest nutritive value. Good as our winter rations, containing silage, are known to be, the fact remains that winter-fed cows respond to pasture feeding, in the spring, out of all proportion to the caloric value of the green grass ingested. The animals invariably respond in milk production, physical condition, and smoothness of coat. Investigations of our winter dairy rations should assist in improving this situation. Similar studies should be made on many of our commercially prepared foods.

It has already been indicated that heat undoubtedly possesses a destructive action but oxidation seems to be an equally important factor. Drummond[9] and his co-workers point out that this is one reason why lard is usually devoid of vitamine A. They contend that the small amount of vitamine that is normally present in lard is destroyed in commercial rendering processes.

In the light of our present knowledge, proper desiccation, with a minimum of air and a high temperature for a short time, should be advantageous. We have little or no knowledge of the influence of humidity, acidity, alkalinity, concentration of sugars, etc., during the drying process.

Some investigators find no antiscorbutic value in certain condensed milks. Hume[17] reports that condensation by the vacuum pan method had no effect upon the antiscorbutic properties of a sample of milk under investigation at the Lister Institute. Professor Combs, Miss Francis, and the writer are now investigating this question further, at the Pennsylvania State College. We are making several types of condensed and evaporated milks by means of the Ruff evaporator, which employs a blast of air through the heated milk. We are comparing the vitamine content of this milk with the fresh raw milk and with the same milk condensed in a commercial vacuum pan.

As far as vitamine destruction is concerned, we have little to fear in our ordinary cooking processes unless the length of time of cooking is excessive. The water-soluble vitamine seems to be more stable to heat than either of the others, although it is destroyed by long-continued heating or by autoclaving. Even when some vitamine destruction occurs, there is every reason to believe that there is seldom danger of a vitamine deficiency. Neither is there much to fear in commercial pasteurization of milk, provided the usual method of vat pasteurization is employed. Granting that some vitamine destruction takes place in many of our commercial processes, there seems to be no reason for being unduly disturbed, providing the diet is not restricted, for long periods, to foods thus treated. Such foods are of great value and their manufacture must not be discouraged. We must simply recognize their deficiencies and supplement these deficiencies with other foods. Our work on milk also lends support to the practice of "short-time boiling" of milk advocated by Lane-Claypon[18] and many pediatricians.

We must admit that our investigational methods are far from satisfactory. Our best planned work in many instances is only roughly quantitative, but the results obtained in the ten or twelve years of vitamine research have repaid their financial cost many times.

The applications of vitamine research to the feeding of malnourished children in Europe, and especially in Vienna, by Miss Chick and her co-workers, is one of the best examples of the practical value of this branch of nutritional science.

Bibliography

1—V. Furst, *Z. Hyg. Infektionskrankh.*, **72** (1912), 121; H. Chick and E. M. Delf, *Biochem. J.*, **13** (1919), 199; B. Cohen and L. B. Mendel, *J. Biol. Chem.*, **35** (1918), 425; J. F. McClendon, *Ibid.*, **40** (1919), 243.

2—H. W. Wiltshire, *Lancet*, **1918** [II], 811.

3—H. Steenbock, *Science*, **50** (1919), 352; H. Steenbock and P. W. Boutwell, *J. Biol. Chem.*, **41** (1920), 81, 163; **42** (1920), 131; H. Steenbock and E. G. Gross, *Ibid.*, **41** (1920), 149.

4—L. S. Palmer, *Science*, **50** (1919), 501; L. S. Palmer and C. Kennedy, *J. Biol. Chem.*, **46** (1921), 559.

5—J. C. Drummond and K. H. Coward, *Biochem. J.*, **14** (1920), 668.

6—M. Stephenson, *Biochem. J.*, **14** (1920), 715.

7—A. F. Hess and L. J. Unger, *J. Biol. Chem.*, **38** (1919), 293.

8—T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **39** (1919), 29.

9—J. C. Drummond, J. Golding, S. S. Zilva and K. H. Coward, *Biochem. J.*, **14** (1920), 742.

10—R. A. Dutcher, C. H. Eckles, C. D. Dahle, S. W. Meade and O. G. Schaefer, *J. Biol. Chem.*, **45** (1920), 119.

11—E. B. Hart, H. Steenbock and N. R. Ellis, *J. Biol. Chem.*, **42** (1920), 383; A. F. Hess, L. J. Unger and G. C. Supplee, *Ibid.*, **45** (1920), 229.

12—A. Harden, *Lancet*, **1918** [II], 320; E. M. Delf, *Biochem. J.*, **14** (1920), 211; V. K. LaMer, H. L. Campbell and H. C. Sherman, *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 122; A. F. Hess and L. J. Unger, *Ibid.*, **16** (1919), 52.

13—F. G. Hopkins, *Biochem. J.*, **14** (1920), 725.

14—A. F. Hess and L. J. Unger, *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 143.

15—S. S. Zilva, *Biochem. J.*, **14** (1920), 740.

16—J. C. Drummond and K. H. Coward, *Biochem. J.*, **14** (1920), 734.

17—E. M. Hume, *Biochem. J.*, **15** (1921), 163.

18—Janet E. Lane-Claypon, "Reports to the Local Government Board on Public Health and Medical Subjects" (London) (New Series **63**).

Standardized Methods for the Study of Vitamines

By A. D. Emmett

MEDICAL RESEARCH LABORATORY OF PARKE, DAVIS AND CO., DETROIT, MICHIGAN

The enormous amount of work that has been reported in the past few years upon studies relating to the vitamines has brought about a marked increase in interest in some lines of biological and food chemistry. As one carefully studies the many scientific papers on vitamines, he is impressed with the idea that the general plan of carrying out the investigations has been more or less characteristic or provincial with certain laboratories. That is, there is often such a difference between the basic plans for executing the experiments that the results of similar studies reported by the several workers are generally not comparable. It is, therefore, evident that the conclusions will not be consistent at times, and also that a certain amount of confusion as to the relative vitamine content of this or that substance will be produced.

It is natural perhaps that such a condition of affairs should have arisen. For as long as we know so little about the chemical nature of the vitamines, and our chemical methods for isolating them are so meager, we must of necessity be dealing with extracts which are a mixture of substances. Then, too, having to rely upon the biologic feeding method, where the animal, food and environmental conditions should be under exact control, one readily realizes how fundamentally important and how difficult it is to obtain accurate results at all times. It is thus easy to see that unless there is some definite understanding as to details of procedure, many variables may probably be introduced by each laboratory working on the subject.

To the writer's mind, it is imperative that something should be done to modify this condition; otherwise what is being reported upon the vitamine content of such substances as foods and vitamine products will need to be revised very considerably later on. These statements are not intended to imply in the least that the results thus far obtained are not of extreme value.

Considerable time and effort have been put forth to devise quantitative methods for measuring the vitamines in extracts made from foods. Various forms of animal and plant life have been employed. Thus, Emmett and Allen[1,*] tried the tadpole; Chambers,[2] the paramecium; and Williams[3] and Bachmann,[4] the yeast. The yeast method as suggested

---

[*] Numbers in text refer to Bibliography, p. 1106.

by Williams for measuring the antineuritic vitamine has shown the most promise.[5] However, the objections to it that have been put forth are of such a nature that it would seem that further reports will be needed before the desired confidence can be placed in it.[6]

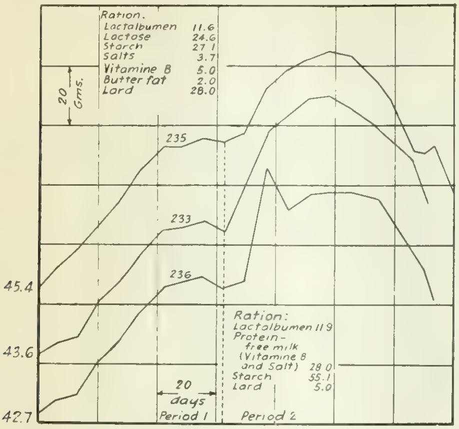


FIG. 1—The curves show how one may be misled by changing too many factors in the diet and then not running the test over a long enough time. The diet in Period 1 was slightly below the normal for growth, being low in fat-soluble A. In Period 2 for the new diet, all the fat-soluble A was left out, the amount of starch was increased, the fat was reduced, and new sources of water-soluble B vitamine and mineral salts were used. The rats began to gain following the change, instead of making the expected decline. This was undoubtedly due to the alteration in texture and palatability of the diet. Later, after 35 days, the rats lost in weight and developed the usual symptoms of xerophthalmia, etc. Similar conditions might result if one food were substituted for another in part or whole.

We are, therefore, still forced to rely upon the more laborious biologic method, which involves the feeding of animals, as the most dependable and safe guide. In fact, for some time, apparently, this method will have to be resorted to in the last analysis where any reasonable doubt exists.

In view of this fact, the suggestion might, therefore, be made that we endeavor to adopt a plan whereby it would be feasible to profit by the very valuable work done thus far and to carry out a series of coöperative feeding experiments so as to establish a more uniform scheme for the study of vitamines. This should be done with the idea of working toward standardizing some methods which in turn could be adopted provisionally. From the experience gained in working along nutritional lines for over fifteen years, the past five of which have been devoted to vitamines in particular, it would seem to the writer that there is much to be gained by following out such a program. It would serve as a helpful guide in determining when one has acquired sufficient knowledge of the technic to feel confident of the accuracy of his results. In this way alone it would be of great value to research workers and to the control departments of some of our industrial laboratories.

POINTS TO BE CONSIDERED

In line with this suggestion a few points may be brought out to emphasize this need and point to some plans that might be considered:

1—There should be a strict uniformity in the basal diets. Thus, in the case of the growing rat, we should agree upon a basal diet that is complete for normal growth and reproduction; upon one deficient only in the water-soluble B vitamine, and upon one deficient only in the fat-soluble vitamine or vitamines. And in the case of the guinea pig, we should have a complete basal diet and one deficient in the water-soluble C. In these diets, it should be understood that the percentage of protein, carbohydrate, fat and mineral salts, and the kind and quality of these nutrients should be the same throughout, for the particular purpose intended. That is, all laboratories should use exactly the same basal diets.

It would then be possible always to employ these rations for the normal and pathological control groups and then to compare with these control findings, the results obtained from any other combination of nutrients that seemed desirable in connection with a particular phase of a vitamine project that one might have under way. That is, if the control data obtained from these basal diets were always reported along with the experimental results, it would be easier to interpret and compare the conclusions from different workers.

2—In the preparation of these basal diets, definite methods should be outlined, with respect to detailing just how to purify the various constituents used—the proteins, carbohydrates, fats, and mineral salts. Besides, exact methods should be given for preparing the vitamine extracts that are to be incorporated. Then again, it should be stated clearly how and in what order these ingredients are to be combined; for unless this is done the texture of the ration will often vary considerably, and thereby an unintentional error will be introduced which might affect the food consumption, and this in turn might influence the trend of the weight curves, etc.

3—It is equally important that there be some definite statements made with respect to the experimental animals. In the case of rats and guinea pigs, the age, weight, sex, and exact physical conditions should be carefully observed and stated. It is known, for example, that, for the best comparisons, the animals should be of about the same age and weight at the start, and that younger rats are preferable to older ones. In our own work where we have used some 2000 pigeons, we find that it is necessary to consider breed, previous feeding, age, body conditions, weight, season of the year, etc., in order to obtain the best results in testing for the antineuritic vitamine.

Also, in the case of handling and taking care of the animals, it is essential to bear in mind that one should avoid exposing them to sudden changes in temperature and to undue excitement, and to too much handling. Systematic attention should be given to cleaning and disinfecting the cages, bedding,

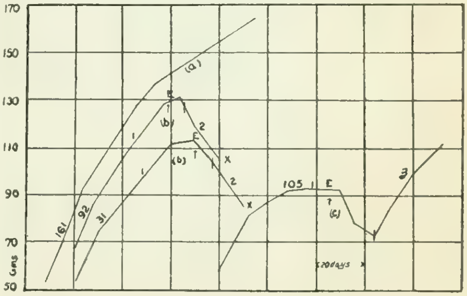


FIG 2—The curves show that when the diet was varied but slightly the resultant effect was more nearly in accord with the predictions. Curve *a* contained all the nutrients for normal growth. Curves *b* lacked the fat-soluble A vitamine. In the latter part (2) of this curve, fat devoid of this vitamine was introduced by substituting it for an equal amount of lard. No change occurred. Curve *c* also lacked the fat-soluble A, but later the fat was introduced which contained this vitamine. Increased growth took place along with the correction of xerophthalmia.

food cups, and water receptacles. Vermin or lice should be scrupulously excluded. Special care should be given an animal when it becomes appreciably affected by the deficiency disease, and so on. In fact, it is only after considerable experience that one can always be sure the effect of the experimental diet is a bigger factor than some of the other variables that may have been introduced.

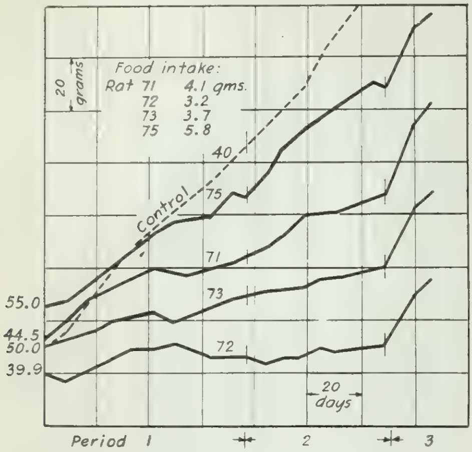


FIG. 3—The curves illustrate how it is sometimes necessary and essential to correlate the food intake with the weights. Here the weight curves followed almost in the same relation as the food intake. Rats 71 and 75 ate the most, and gained better than rats 72 and 73 which ate less.

Similar results were obtained by Osborne and Mendel[7] in feeding raw and cooked soy beans. The rats practically declined to eat the raw food and hence made no gains, while they ate the cooked food readily and grew normally.

4—It is very important to state whether the animals are to be force-fed or not; whether the food-intake is to be accurately recorded or not; whether the rations are to be made frequently or in large enough quantity to last for a considerable time; whether the consistency of the food or ration is appreciably altered when the changes in the diet are made, and, if vitamine extracts are to be used, whether the animals are to be treated during the test period, or fed at this juncture a mixture of the basal diet and the extract.

5—In the feeding, the question arises whether the rations should be tested from the standpoint of a prophylactic or a corrective. That is, should the test be one of preventing the usual decline in weight, etc., that comes about from the absence of the particular vitamine, or should it be one endeavoring to bring about a normal response after the animal has become affected? In many ways, it is often preferable to follow the latter method.

6—It is very important that the tests should be run long enough to be conclusive. We have had instances in the case of the rat, where the pathological animals did not respond quickly when put upon a curative diet. Sometimes they did not manifest any signs of improvement for almost a week, when they began to show the effects of the new diet. Here it is not a case of the vitamine being absent but simply a question of the animals not eating the new ration at first. When they do begin to take the food, the effect of the treatment will become very evident. However, the precaution should be taken to make sure that any gains in weight are not due simply to a change in the physical nature of food, rendering it possibly more palatable. Noting the physical condition of the animal and continuing the test long enough will settle this point. Where it is possible, as in using extracts, it is generally much better to keep the basal diet the same throughout and to give the animals definite doses of the extracts. In this way, one can make sure that the material has been consumed. This, of course, cannot be done where one wishes to test a food in its entirety.

RECOMMENDATION

From the six points that have been elaborated upon, it would seem very evident that there is an excellent opportunity and a real need for formulating some definite working plan which would be a practical aid in making it easier to carry on studies and experiments relating to the vitamines. Many of these possible irregularities could thereby be eliminated to some degree to advantage. The adoption of some such suggestion would aid very materially in clarifying certain questions that are coming up with the rapid advancements on this subject.

This plan could be accomplished if five or more laboratories that are seriously interested in vitamines would come to some mutual agreement regarding what methods seem most plausible and easy to carry out. Each should be asked to follow very carefully definite recommendations as to basal diets, animals, methods of feeding, etc. In fact, it might be best to go still further, in the beginning, and make up a large supply of the basal rations and to send portions to each investigator to use in accord with certain directions. In turn, the results obtained could be collected and studied to determine how closely the laboratories agreed.

These data would be of immense value and they might immediately settle and help to establish some very essential and fundamental facts. For one thing, the results would make it possible to determine what allowance should be made for the technic and personal factors that enter in. Also a number of points as to the exact pathological conditions that are brought about could be more clearly established.

Having thus obtained some fair knowledge of the range of experimental expectation that one may figure upon, it would then be possible to elaborate the procedure in any way that the individual project might suggest. However, even then the number of variables introduced at any stage in the experiment should be few enough and in such sequence that proper deductions would be possible.

This plan would seem to be a logical one at this stage in the development of the subject. It would be to the best interest of those who are in charge of research and control work on vitamines; it would help to add greatly to the valuable facts that are already at hand on the etiology and pathology of the deficiency diseases; it would make it possible to come to a much more definite conclusion as to what foods or food products are rich or poor in certain of the so-called vitamines, and would assist appreciably, in general, in obtaining fairly definite relative values.

BIBLIOGRAPHY

1—A. D. Emmett and F. Allen, *J. Biol. Chem.*, **38** (1919), 325.

2—M. Chambers, *Biol. Bull.*, **36** (1919), 82.

3—R. J. Williams, *J. Biol. Chem.*, **38** (1919), 465; **42** (1920), 259.

4—F. M. Bachman, *J. Biol. Chem.*, **39** (1919), 235.

5—W. H. Eddy and H. C. Stevenson, *J. Biol. Chem.*, **43** (1920), 295; C. Funk and H. E. Dubin, *Ibid.*, **44** (1920), 487; F. K. Swoboda, *Ibid.*, **44** (1920), 531; M. Ide, *Ibid.*, **46** (1921), 521.

6—A. D. Emmett and M. Stockholm, *J. Biol. Chem.*, **43** (1920), 287; G. de P. Sousa and E. V. McCollum, *Ibid.*, **44** (1920), 113; E. I. Fulmer, V. E. Nelson and F. F. Sherwood, *J. Am. Chem. Soc.*, **43** (1921), 186, 191; M. B. MacDonald and McCollum, *J. Biol. Chem.*, **45** (1921), 307; **46** (1921), 525; V. E. Nelson, E. I. Fulmer and R. Cessna, *Ibid.*, **46** (1921), 77; W. H. Eddy, H. L. Heft, H. C. Stevenson and R. Johnson, *Ibid.*, **47** (1921), 249; A. Harden and S. S. Zilva, *Biochem. J.*, **15** (1921), 438.

7—T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **32** (1917), 369.

Vitamines from the Standpoint of Structural Chemistry[1]

By R. R. Williams

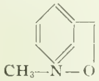
ENGINEERING DEPARTMENT, WESTERN ELECTRIC CO., NEW YORK, N. Y.

β-HYDROXYPYRIDINE

Previously published papers[2] have recorded the fact that β- as well as α-hydroxypyridine exists in two crystalline modifications. Dr. H. E. Merwin of the Geophysical Laboratory kindly examined a preparation and describes the two crystal forms as follows:

> The preparation contained crystals of two very different habits; crystals having one habit were lath-shaped with parallel extinction; γ, parallel to the long axis, equals or slightly exceeds 1.74; β, parallel to the intermediate axis, equals 1.600; and α, parallel to the short axis, is slightly greater than 1.575, but much less than 1.60. The crystals, therefore, are orthorhombic, with a small positive optic axial angle.
>
> Crystals having the other habit were equidimensional and possessed some well-formed faces, but the optical orientation could not be determined. They are optically positive, with moderate optic axial angle. $\alpha =$ or is slightly < 1.174, γ is slightly < 1.735.
>
> A few of the lath-shaped crystals were partly changed into aggregates of small crystals having α and γ like those of the equidimensional crystals. By warming the lath-shaped crystals on a slide somewhat below 100° this transformation in the solid state could be brought to completion within a few moments. Although the optical properties of the two kinds of crystals are so similar, there is no doubt that they are different forms.

β-Hydroxypyridine has heretofore been regarded as enolic, differing sharply from the α and γ isomers. This is not the case, for by titration with bromine[3] all three prove to be non-enolic in neutral solution, though largely enolic in sodium ethylate solution. The α and γ isomers have been shown to form both oxygen and nitrogen ethers,[4] but this was held to be impossible in the case of β-hydroxypyridine. As predicted in a previous paper,[5] β-hydroxypyridine forms a nitrogen-methyl ether which has the structure



thus establishing the complete parallelism of the β- with the α- and γ-hydroxypyridines. This nitrogen ether of β-hydroxypyridine is prepared from methyl iodide addition product[6] by shaking in aqueous solution with silver oxide. After filtration from silver iodide the solution is saturated with potassium carbonate. The supernatant oil which separates is dried over anhydrous potassium carbonate and distilled *in vacuo* (b. p. 300° at 2 mm.). The viscous oil is miscible with water in all proportions; nonvolatile with steam; reduces permanganate instantaneously and gives a white, crystalline precipitate with mercuric chloride; when decomposed in aqueous solution with sodium amalgam it yields copious amounts of primary amine, as shown by mercuric bromide. In all respects it resembles the α and γ nitrogen-methyl ethers and not the oxygen ethers. Analysis by Kjeldahl-Gunning-Arnold method gave 12.68 per cent nitrogen (calculated 12.85 per cent).

FEEDING EXPERIMENTS

Although the foregoing constitutes a definite contribution to the chemistry of the hydroxypyridines, no such decisive answer is possible as to their resemblance to vitamine B. Harden and Zilva[1] have failed to confirm the writer's findings as to the physiological action of α-hydroxypyridine. Their statements are not altogether convincing that the active form was actually administered or that the birds were well chosen for experiment. However, it must be conceded that the positive evidence of antineuritic action is equally unconvincing, inasmuch as no prophylaxis has been obtained with the substance. A protective feeding experiment is of vastly more value than numerous curative tests and such evidence must be forthcoming if it is to be beyond dispute.

Curative tests were made with a variety of substances and the results of some of them are recorded below.

SUBSTANCE	BIRDS TREATED	DOSE IN MG.	RESULT
Anthranil	5	1	Evidence of toxicity
Benzo-orthoxazinone	8	2–5	No improvement
β-Hydroxypyridine (mixture of 2 forms)	10	2	6 partly relieved 4 unaffected
β-Methylpyridone	5	2	4 substantially improved
Picolinic acid methylchloride	5	2–5	No effect

Protective feeding experiments have been made with a large variety of synthetic substances, including in addition to those used for curative tests the following: vicine, divicine, 6-oxypyrimidine, trimethyluracil, amino-trimethyluracil, dialuric acid, tetramethyl uric acid, methoxy caffeine, 1, 3, 7-trimethyl uric acid, isocytosine, and 4-phenylisocytosine. Only trimethyluracil and 4-phenylisocytosine gave any suggestion of protective effect.

4-PHENYLISOCYTOSINE

The writer's experience with 4-phenylisocytosine is as follows:

Following the directions of Johnson and Hill,[2] an attempt was made to prepare the four modifications described by them. Preparations were obtained which appeared to agree fairly well with three of the four isomers described by Johnson and Hill, but at no time was the fourth and most unstable form discovered. Its existence is by no means disputed, as experience with the various forms clearly indicated that apparently trivial modifications of method were sufficient to alter the result. The problem appeared baffling in the extreme. For example, β and γ forms, having the same melting point and identical crystallographic and optical properties as far as they could be measured, still differed from one another in that the β was approximately ten times as soluble in alcohol as the γ form. It was found impossible precisely to correlate crystal form with method of preparation, much less with physiological action.

A test was made by daily administration by mouth of 5 mg. of freshly prepared 4-phenylisocytosine to eight pigeons fed on a white rice diet. Four birds received preparation B and four preparation D, corresponding in appearance to Johnson's and Hill's β and δ forms. The birds were picked at random from the same group and the experiments were carried out simultaneously and side by side. All four birds given preparation B lost weight less rapidly than any of the four receiving preparation D. The result is precisely what would be expected if preparation B had contained a small amount of an antineuritic so unstable that it passed out of existence in the course of a few days. An experiment with the two identical preparations indicated no physiological difference two months later.

Whether this result or any of the physiological results so far obtained with synthetic substances has any real significance must be left to the reader's judgment. However, the solubilities, chemical reactions, and natural occurrence of vitamine B, so far as known, agree very closely with the pyrimidine bases, a class of substances known to be capable of a very delicate desmotropism. In view of these facts any suggestion of physiological activity in synthetic preparations of this group or its allies ought not to be lightly dismissed. The writer believes that vitamine B eventually will be found to be a cyclic nitrogen compound with an oxygen substitution in the ring and capable of existence in a betaine configuration. If the work on synthetics offers any useful suggestions as to manipulation in the isolation or identification of the vitamine from natural sources it will have served an adequate purpose.

---

[1] The work here recorded was largely done at the Bureau of Chemistry. It was interrupted by the war, and as no early opportunity to resume it can be foreseen the series of papers is closed with this record of some of the incomplete work which seemed most likely to be useful.

[2] R. R. Williams, *J. Biol. Chem.*, **25** (1916), 437; **29** (1917), 495.

[3] K. H. Meyer, *Ann.*, **380** (1911), 212.

[4] H. v. Pechmann and O. Baltzer, *Ber.*, **24** (1891), 3144.

[5] R. R. Williams, *J. Biol. Chem.*, **29** (1917), 495.

[6] Fischer and Renouf, *Ber.*, **17** (1884), 763, 1896.

[1] *Biochem. J.*, **11** (1917), 172.

[2] *J. Am. Chem. Soc.*, **36** (1914), 1201.

Vitamines from the Standpoint of Physical Chemistry

By Victor K. LaMer

Department of Chemistry, Columbia University, New York, N. Y.

To cover the subject of vitamines in detail from the standpoint of physical chemistry would require more time than has been allotted and for that reason the discussion will be limited to an outline of the subject, dwelling in detail only upon the more important phases. For the same reason the assumption is made that we have a quantitative method for measuring the vitamines in question, a method in which we know approximately at least the errors with which our measurements are burdened.

Granted that we have such a method, it then becomes feasible to interpret the data in the light of physical chemistry. This procedure promises results of practical value to the manufacturer of food products, who desires information in regulating his process so that he may obtain the maximum preservation of vitamines consistent with the other requirements of the process, and in addition it furnishes data of theoretical value which should aid us in establishing what the chemical structure of the vitamine may be and may not be.

The courses which these investigations have taken may be outlined as follows:

1— Studies on solubilities in different media.

2—Studies on the adsorption of vitamines under varying conditions.

3— Studies on the size of the particles which carry the vitamine activity, or more specifically studies on ultrafiltration.

4— Studies on the stability of the material under conditions in which time, temperature, hydrogen-ion concentration, radiant energy, and oxidizing agents are the independent variables.

For the most part studies made with these objects in view have appeared in the form of short, disconnected communications, from which it is difficult to interpret the results obtained because of variations in technique, but more often because some one of the variables just mentioned has not been controlled.

Solubility Studies

That the science is urgently in need of more uniform and quantitative measurements becomes apparent when we discuss solubility. The early studies on solubility led to the distinction in the vitamines; namely, A, B, and C. Later and more exacting studies have shown that this is but a rough method of classification and that the solubilities given refer only to the more characteristic solubility. The fat-soluble vitamine A in skim milk is a case in point. Some workers have tacitly considered that diets containing skim milk were free from vitamine A, since this vitamine is soluble in fat solvents. Experiments by McCollum, and later by Sherman, MacLeod and Kramer,[1] have shown that this assumption is false and that the amount of vitamine A in skim milk is roughly equal to that contained in the fat layer. When this result is interpreted in the light of the distribution law (since equilibrium exists between the phases) it will be seen that the ratio of the solubility of the vitamine in the oily phase and the aqueous is about 30 to 1. It is very likely that further studies would reveal a similar state of affairs for the other vitamines. For instance, Meyers and Voegtlin[1] have recently reported water-soluble B to be somewhat soluble in fat oil.

Adsorption Studies

Adsorption studies have been confined almost entirely to the type of experiments of Harden and Zilva,[2] who showed that the B vitamine was adsorbed by fuller's earth and dialyzed iron, while the C vitamine was not appreciably affected under the conditions of their technic. The authors rightly point out that the completeness of the adsorption is especially sensitive to changes such as H-ion concentration, so that it is necessary in reporting experiments of this type that all conditions be expressly stated. The claim of Ellis, Steenbock and Hart[3] that blood charcoal removes a measurable amount of the C vitamine from orange juice shows that the separation of B and C by this means is not quantitative.

Studies on Ultrafiltration

The same investigators have studied the effects of ultrafiltration and conclude that there is likewise a partial retention of vitamine C when Chamberland candles are used. It is well to emphasize that the nature of the pores and the character of the filtering material are important factors in such procedures. The recent work on colloids indicates more and more that the process of ultrafiltration, although it may give a crude measure of the size of particles, is far from being a simple case of mechanical separation and that instead the relative chemical nature of the material and the filter bag have much to do with the process.

Studies on Stability

Investigations upon the stability of the vitamines has received considerably more attention than have any of the types of investigation just mentioned, due very largely to the more practical aspects of such studies.

Strictly speaking,[4] the use of the term stability should not be applied to vitamines at present because this term refers solely to the effect of energy, usually in the form of heat, upon a substance, while the latter is carefully isolated from all other substances. The effects of the other components of the environment should be referred to as separate chemical properties. It is obvious then that we can speak of the stability of the vitamines only when we are careful to define the conditions under which the experiments are carried out.

Two years ago the writer, in conjunction with Professor H. C. Sherman and Miss H. L. Campbell of the Laboratory of Food Chemistry at Columbia, began research upon the stability of the antiscorbutic vitamine.

At that time it appeared from the work of Holst and Frohlich,[5] Delf,[6] and Hess,[7] that the destruction of the antiscorbutic vitamine could be expressed as some function of the temperature, the time of heating, storage, and the acidity. Since then it has become very evident that we must consider still other factors, such as the oxidation and reduction potential of the solvent medium, and perhaps the effects of radiant energy. It is the purpose of this paper to show as far as possible how these factors are related to one another.

[1] *Proc. Soc. Exptl. Biol. Med.*, **18** (1920), 41.

[1] *J. Biol. Chem.*, **42** (1920), 199.

[2] *Biochem. J.*, **12** (1918), 93.

[3] *J. Biol. Chem.*, **46** (1921), 367.

[4] Alexander Smith, "Inorganic Chemistry" (new edition), p. 149.

[5] *Z. Hyg. Infectionskrankh.*, **72** (1912), 1.

[6] *Biochem. J.*, **12** (1920), 416.

[7] Hess and Unger, *J. Biol. Chem.*, **48** (1918), 297.

RELATION OF TIME OF HEATING TO TEMPERATURE

It was felt that the relative importance of the time of heating to the temperature of heating was the most important relation of all and accordingly the first experiments were made with the object of determining the functional relationship which existed between them. Comparisons were made of the quantities of antiscorbutic vitamines, given in the form of filtered canned tomato juice that were necessary to protect guinea pigs against varying degrees of scurvy, when the tomato juice had been heated from 1 to 4 hrs. at 60°, 80°, and 100° C. From the data obtained it is easy to calculate the per cent destruction for each animal, the average of the results of four or more animals being accurate to ±5 per cent. Inasmuch as the results of these investigations are being published in detail elsewhere, reference will be made here to only the more important conclusions.[1]

In the first place, the data show that the destruction of the antiscorbutic vitamine is of the nature of a chemical reaction in which the velocity is accelerated by increase of temperature. The velocity of the destruction reaction decreases with the progress of time in greater degree than does a reaction of the first order. Two explanations exist. Either the reaction is of a higher order, or another variable parameter is complicating the reaction under long-continued heating (4 hrs.). This phenomenon of flattened reaction velocity curves is not an uncommon one in reactions involving a complicated substrate such as we have in the hydrolysis of protein by pepsin. It has been found that the per cent destroyed at 60°, 80°, and 100° C. can be represented by the empirical equation

$$X = K\sqrt[5]{t}.$$

When t is the time expressed in hours, the values of K become 0.26, 0.39, and 0.49 for the temperatures of 60°, 80°, and 100° C., respectively. X = per cent destruction of the vitamine.

These values for the velocity constants show that the temperature coefficient of the reaction is below that of most ordinary chemical reactions, which are doubled or trebled for a 10° rise in temperature. Q_{10} has the low value of 1.1_3 between 80° and 100° and the value 1.2_3 between 60° and 80° C. These data exclude the possibility that vitamine C is of a protein- or enzyme-like nature.

While discussing the destruction of vitamines at low temperatures, particular attention should be called to the fact that merely measuring the amounts of vitamine extracts fed does not in itself constitute a quantitative determination for it is obvious that if the experimental animal is given more than it needs, efficiency effects will not be observed and the result will not be an accurate measure of the amount of vitamine given. It is only when quantities at or below the minimal protective dose are used that we are justified in drawing conclusions regarding the extent of destructive agencies.

Chick and Hume[2] have previously discussed this point, but their criticism has not been heeded by many of our American workers. The most recent violation of this principle appeared in a paper by Dutcher, Harshaw and Hall,[3] where the conclusion is drawn that no destruction of antiscorbutic vitamine occurs when orange juice is heated for 1 hr. at 63° C., a statement in conflict with the data just given for tomato juice. The writers of the article reach this conclusion from experiments in which only one level of intake is studied. The experiments show that the protective effect of 3 cc. of heated orange juice is practically the same as that of 3 cc. of unheated juice, as would be expected, since the minimal protective dose of orange juice, as redetermined by Davey,[1] is 1.5 cc., a value which is in conformity with Delf's earlier experiments. From these figures it is plain that any destruction under 50 per cent would not be observed when 3 cc. was the smallest quantity fed, but if both the heated and the unheated orange juice had been fed at a level of 1.5 cc., the results would doubtless have indicated a destruction comparable to the 25 per cent destruction we have observed in tomato juice under very similar conditions.

ACIDITY—Our studies on the effect of heating at reduced H-ion concentrations show that this results in an increase in the velocity of destruction. Thus 50 per cent is destroyed at the natural acidity, pH 4.3; when the organic acids are somewhat less than half neutralized, or pH = 5.2, the destruction is 58 per cent; at complete neutralization, or pH = 8.3, the destruction is about 62 per cent, the time and temperature being 1 hr. and 100° C. Further it was shown that the destruction was increased when the material was not reacidified back to the original acidity after heating, as was done in all of the cases just mentioned. Thus when the material was left alkaline and stored at 10° C., and fed over a period of 5 days, the destruction amounted to as much as 95 per cent.

TABLE I

No. of Animals	pH	RESULT
		Oxygen bubbled through
4 3	4.3 8.3	Complete destruction. Acute scurvy in all cases, the animals dying within 27 to 38 days
		Hydrogen bubbled through
3	4.3	Some protection—life prolonged to 42 and 56 days. One animal still living on the 56th day
3	8.3	Some protection. Life prolonged to 31, 46 days. One animal living at 56th day but very scorbutic
		Air expelled before heating
12	4.3	50 per cent destruction } Life prolonged to 90 days or over
5	8.3	62 per cent destruction }

OXIDIZING AND REDUCING AGENTS—To test the effect of oxidizing agents, tomato juice was put into flasks fitted to reflux condensers to prevent evaporation, the flasks were immersed in a boiling water bath, and either oxygen or hydrogen was bubbled through the juice. Since the oxidizing potential of oxygen and the reducing potential of hydrogen vary with the H-ion concentration, the tomato juice was tested both in acid and slightly alkaline solution and the results compared with our previous experiments, in which the air was first expelled by the water vapor coming from the boiling solution and a cotton stopper introduced to prevent re-access of air during the heating period. The results of preliminary experiments upon 13 animals fed at the levels of 2, 3, and 4 cc. are given in Table I.

While it would not be wise to draw too definite conclusions from the number of animals used, the concordance in the results makes one feel safe in concluding that the velocity of the reaction under the oxidation potential furnished by a saturated solution of oxygen in both acid and weakly alkaline solution is sufficiently rapid to destroy the vitamine completely in 1 hr. at 100° C.

We are inclined to interpret the other results as indicating that vitamine C is susceptible to a pure heat destruction, which may be increased by the addition of oxidizing or reducing agents, since somewhat greater destruction occurred when hydrogen was bubbled through when compared to the cases where no gas was used.

This interpretation makes it entirely possible that the heat destruction of vitamine C is of the nature of an intramolecular oxidation and reduction, such as occurs when aldehydes or sugars are heated, especially in alkaline solution (*i. e.*, Cannizzaro reaction), and the addition of external oxidizing or reducing agents simply serves to carry the equilibrium point of the reaction more in one direction or the other, thus increasing the velocity.

---

[1] LaMer, Campbell and Sherman, *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 122; *J. Am. Chem. Soc.* (in press).

[2] *J. Biol. Chem.*, **39** (1919), 203.

[3] *Ibid.*, **47** (1921), 483.

[1] *Biochem. J.*, **13** (1921), 83.

It is our intention to continue this study on the destruction of vitamine under the influence of experimentally measured oxidation and reduction potentials as soon as conditions permit.

The Antiberiberi Vitamine

By **Casimir Funk**

Research Laboratory, H. A. Metz, New York, N. Y.

The antiberiberi or B vitamine is the most important and the most frequently studied of this class of substances. Its discovery was contingent, as is well known, on the elucidation of the etiology of beriberi, a far-eastern disease, due to continuous consumption of polished rice. This vitamine is more or less distributed throughout the whole animal and vegetable kingdom, but in the cereal grains it is located chiefly in the germ and in the peripheral layers and therefore easily lost during the cleaning process applied to the grain.

As regards the function of this substance in the body, we know only that in its absence from the food general cachexia develops, similar to a severe inanition, the whole picture originating, as it seems, in the involvement of the central nervous system. Among the more important pathological changes is the increase in size of the suprarenals, going hand in hand with an increased adrenaline output. This observation put forward by McCarrison applies for the time being only to avian beriberi and may be brought into relationship with the present writer's observation that an increased carbohydrate consumption hastens the onset of the disease, showing perhaps that B vitamine plays a role in the carbohydrate metabolism. Contrary to this, a higher protein supply diminishes the needs for this vitamine and acts as a vitamine saver.

The present paper will deal briefly with the chemistry of B vitamine. The chemical studies deal almost exclusively with rice-polishings and, particularly, yeast, and were started about ten years ago. In dealing with this phase of the subject, very serious experimental difficulties were encountered, owing to the fact that no precipitation or color reaction specific for B vitamine is known. This substance is present in the starting material in minute quantities (as far as our present evidence goes, there is no more than a fraction of a milligram in a pound of dried yeast) and has to be separated from a large amount of inactive material, which is only partly becoming chemically known to us. The first endeavors were therefore directed toward a separation of the active material by the simplest possible procedure. Limiting the steps to a minimum is very important for the final success, as the time taken for the operations is an important factor in obtaining the final fraction in an active state. This separation was effected first by an extraction with alcohol, then by precipitation with phosphotungstic acid, tannic acid being used for the same purpose by Suzuki. Later came the adsorption with fuller's earth, introduced by Seidell, then the alcohol precipitation method of Osborne and Wakeman, the precipitation with bismuth potassium iodide by Hofmeister, adsorption with norit by Eddy, and so on. Unfortunately none of these methods shows any specificity for B vitamine, and the fractions obtained are contaminated with a large quantity of inactive material. More promising was the method of fractionating the phosphotungstates obtained from yeast by means of acetone, the active fraction being insoluble in this solvent and representing roughly only 10 per cent of the total precipitate.

Isolation of B Vitamine

The isolation of B vitamine was attempted by a number of investigators. In 1911 to 1913, the writer was able, by precipitation of the decomposed phosphotungstates with sublimate, silver nitrate in acid and finally in alkaline solution, to obtain a series of crystalline substances, one of which proved to be nicotinic acid, and another which after recrystallization to a constant melting point still exhibited marked curative properties for beriberi pigeons. These substances were analyzed at that time and their formulas tentatively established, but it is still uncertain whether we were dealing with B vitamine or whether the substance was yet contaminated with adsorbed active material—this in spite of the repeated crystallization. Whatever may be the final outcome, we had in hand a new substance which is worthy of further study. The vitamine research has brought to light a series of new substances, present in the starting materials in very small amounts, among them nicotinic acid, aschamine, and a recently isolated reducing substance, glucathion, obtained by Hopkins. It is clear, therefore, that the above-described attempts did contribute materially, and will do so more in the future, toward increasing our knowledge of chemistry of the living cell. From all the known reactions for B vitamine the most promising for the present is the precipitation with silver in alkaline solution. By using this method we obtain this vitamine in concentrated form, together with other substances which are largely known to us chemically. Among the substances which are carried down in this fraction, we know already the pyrimidines, histidine, histamine, glucathion (peptide composed of glutaminic acid and cysteine), guanidine, carnosine, and nicotinic acid, and we possess therefore ways and means to effect a successful separation of some of the impurities.

By using the combination of his fuller's earth method with the writer's silver method, Seidell was able to obtain a silver fraction which represents a small part of the initial yeast material. As we were able to ascertain in collaboration with Mr. Levy, this fraction contains a large proportion of inactive impurities.

Nomenclature

In concluding the part of this paper relating to attempts at isolation of the B vitamine, the author wishes to dwell a moment on the question of nomenclature. A former assistant, Dr. Drummond, recently suggested dropping the final "e" in the term vitamine. This suggestion did not come as the result of experimental evidence, but merely on theoretical grounds. This may seem a trifling matter, but the suggestion has found already a number of followers. The name vitamine was given in the first place not so much to indicate the amine nature of these substances as for euphonic reasons. We were anxious to choose a name which would "take" and would stimulate workers in this new direction—and it did take. The final "e" was given to indicate the nitrogenous nature of these substances, in which the writer thoroughly believes. After all, the present evidence tends to show that the vitamines act as bases as well as acids and such substances have the ending "e" in the English language. By dropping the "e" very little is changed, the amine still being pronounced. In the absence of experimental evidence against these views, there is little necessity to effect a change of nomenclature at this time. In connection with a possibility of an acidic nature of this substance, we have sometimes succeeded and sometimes failed to distil in vacuum the free ester of the substance which acts on yeast. The experimental difficulty here is in the effective separation of the nondistilling material, which accumulates and causes decomposition at higher temperatures, showing at the same time the complexity of our present vitamine fractions.

Is B Vitamine a Mixture?

Another problem of great interest is whether the substance with which we hitherto have dealt as B vitamine is one or a mixture of substances. For some time, indications have been present in the literature showing that we are dealing here with a mixture. In particular, Abderhalden and Schaumann have contended that there is a substance which acts on the nervous system, another one which acts in maintaining weight. In this country Emmett advocated the view that the substance for rats is not the same as for pigeons and is still different from that which acts on yeast. These views are undoubtedly correct, to a great extent. Recently, in collaboration with Dr. Dubin we succeeded, by fractional adsorption with either fuller's earth or norit, in separating at least two substances in a fairly complete manner. This separation will enable us to study these two substances more closely and also to determine their respective value in animal nutrition. Another field which will be influenced by the above separation is the nature of the substance which is important in the metabolism of lower organisms. Recently, the so-called yeast method was introduced for the quantitative determination of B vitamine. The above separation shows clearly that we are dealing here with two substances at least, one which cures beriberi, and the other which acts on lower forms of life. This second substance we propose to call D vitamine. The yeast method, showing the relative content of extracts in vitamines of the B-type, can no longer be regarded as specific for antiberiberi vitamine. Yeast is favorably influenced by D vitamine and we have no doubt that we are dealing here not with an improvement of the medium, as some workers have contended, but with a specific substance; this presents a new field of investigation for the future. As regards bacteria, the problem is more complicated, as these microörganisms require at least two substances, one present in the blood, possibly connected with the blood pigment, and another substance of the nature of the above-described D vitamine. Here also our adsorption procedure offers a distinct advantage over the methods hitherto employed, as it eliminates a large proportion of the impurities from the start.

LACK OF CHEMICAL KNOWLEDGE

In the chemical work on B vitamine we are still struggling with a difficulty which lies in the way of progress and success. The present methods seem to injure the activity of the substance. This is undoubtedly due to our lack of knowledge of the chemical characteristics of these substances. It seems that in the case of B vitamine we are not dealing, as in the case of other vitamines, with the injurious effect of oxidation. There is something else to be looked for and it seems to the writer that so long as we do not possess a specific precipitation method or know how to stabilize this substance so that one would have the time to study its characteristics, no definite progress can be made. Unfortunately the vitamines, like the rare gases of the air, have so far shown exceedingly little affinity for the known reagents, most of which no doubt have been tried. For the present, therefore, we have to contend with the elimination of impurities; this necessitates slower procedure and we are handicapped by the imperfect chemical knowledge of the latter.

Views are often expressed as to the exaggerated importance assigned to the vitamines. There is no doubt that vitamines do not mean everything in nutrition. One cannot live without vitamines, but one cannot live with vitamines only. There are some who hold that the vitamines are only a fad in science, which will pass away as many other fashions have passed. This is not so; the vitamines are here to stay. Their chemical nature may be difficult to establish, but the price of the efforts will be well worth while. It will open up new viewpoints and bring new ideas. It is therefore a pity that only few organic chemists venture into this field, offering possibilities of new and unexpected developments. For the chemical study of the vitamines, vitamine B, or perhaps better still the above-mentioned vitamine D, offers the best opportunity on account of greater stability. We have to start with the study of the most stable vitamine. Knowing the chemical nature of one such substance, it may prove easier to arrive at the others.

Experiments on the Isolation of the Antineuritic Vitamine

By Atherton Seidell

HYGIENIC LABORATORY, U. S. PUBLIC HEALTH SERVICE, WASHINGTON, D. C.

It is generally acknowledged in recent contributions to the subject that no trustworthy information concerning the chemical nature of any vitamine has, as yet, been obtained. On the other hand, the study of the functions of the several vitamines is progressing rapidly and is closely approaching quantitative exactness in some cases.

The failure to make substantial progress in the chemical isolation and identification of vitamines is due to the length of time required for, and the uncertainties of, the physiological tests available for controlling the fractionations, and more particularly to the readiness with which the characteristic vitamine activity disappears during the laboratory manipulations. In this respect it is a common experience to find that the product finally isolated is devoid of the characteristic physiological action of the original crude material. Some investigators consider it an axiom that the better the final product appears from the chemical standpoint, the worse it will be found when tested for its physiological activity.

It is probable that by far the greater number of the experiments which have been made on the isolation of vitamine are useful principally in showing how the problem cannot be solved and have, therefore, been withheld from publication. A considerable number of the present series are of this type and are omitted. Although those which are given do not furnish a solution to the problem of the true chemical nature of vitamine, they appear to supply another stepping stone toward this goal. A method is described by which a relatively stable silver precipitate, which undoubtedly possesses considerable vitamine activity, can be obtained. It is hoped either that the identity of the active constituent of this product can be established or that the pure vitamine itself may eventually be isolated from it.

The discovery of this new vitamine complex was briefly described in a preliminary paper[1] published several months ago. The reaction involved has since been studied in greater detail and much additional information obtained in regard to it. Briefly, it consists in subjecting a concentrated vitamine extract to successive precipitation with aqueous silver nitrate and ammoniacal silver nitrate. The latter precipitate has been found to contain by far the greater part of the vitamine originally present. Since it is probable that the method of preparing the aqueous vitamine extract used for the precipitation contributes largely to the success of the procedure, this will first be described.

PREPARATION OF CONCENTRATED VITAMINE EXTRACT FROM BREWER'S YEAST

The fresh yeast, as obtained from the brewery, is allowed to autolyze and the thick liquid thus obtained is filtered. English fuller's earth[2] is added to the clear autolyzed filtrate in the proportion of 50 g. per liter and, after thorough shaking, removed by filtration, washed, and dried. This material, called for convenience "activated fuller's earth," is extracted by means of aqueous saturated barium hydroxide solution. The time of contact of the alkaline solution with the solid must be brief. One liter of barium hydroxide solution is used for each 100 g. of the activated solid and the clear liquid, which is separated from the well-shaken mixture, is acidified promptly with a slight excess of strong sulfuric acid. The excess of acid is neutralized by addition of powdered barium carbonate and the milky liquid is filtered. The resulting clear solution is then subjected to lead acetate precipitation and, after filtration, the lead is removed from the filtrate by means of hydrogen sulfide. This final dilute aqueous extract of vitamine is concentrated to a small volume by rapid vacuum distillation. The white amorphous material which separates toward the end is removed by filtration, and the final concentrated extract is reduced to a thick pasty semisolid condition by allowing it to stand several days in a vacuum desiccator.

---

[1] Atherton Seidell, "Preliminary Note on a Stable Silver Vitamine Compound Obtained from Brewer's Yeast," *Public Health Reports*, April 1, 1921, p. 665.

[2] The variety occurring at Surrey, England, and imported by Eimer and Amend.

SILVER NITRATE PRECIPITATION

Of the several factors which modify this reaction, little definite information has been obtained. Furthermore, it is probable that variations in the composition or condition of the vitamine extract exert an influence outweighing all others. Consequently, considerable variations in the appearances and yields of the several fractions may be encountered. In general it has been the custom to conduct the precipitation in relatively small volumes of solution. This was considered to reduce losses due to solubility or hydrolysis of the compounds.

The semisolid vitamine extract obtained from 300 g. of activated solid is usually dissolved in somewhat less than 50 cc. of water and the clear filtered solution precipitated in a centrifuge tube by the dropwise addition, with constant stirring, of a nearly saturated solution of silver nitrate. A curdy white precipitate forms around each drop and its accumulation may finally render the mixture nearly solid. On centrifuging, the supernatant clear liquid is tested for completeness of the precipitation, and when this point is reached the curdy solid is washed by stirring successively with about an equal volume of water, centrifuging, and decanting. During this time the precipitate gradually darkens and may become almost black. In the following pages the precipitate obtained by addition of silver nitrate is designated as (I).

The supernatant liquid and wash water, which give no further precipitate with aqueous silver nitrate, are then precipitated in an exactly similar manner with a concentrated ammoniacal silver nitrate solution. This latter is conveniently made by gradually adding strong ammonia to a concentrated silver nitrate solution until the black silver hydroxide, which at first separates, just redissolves. The curdy precipitate now obtained is similar in volume and appearance to that produced by addition of silver nitrate. It is washed by centrifugation and rapidly becomes dark in color. The precipitate obtained with ammoniacal silver nitrate is hereafter designated as (II).

With vitamine extract made from certain samples of "activated solid" which had become somewhat moldy, no ammoniacal silver precipitate (II) was obtained at this stage. In these cases it was found that precipitate (II) appeared first during the reprecipitation of (I), as will be described in the succeeding paragraphs.

The question as to whether the two precipitates, (I) and (II), should be dried by spreading on a porous plate after this and succeeding reprecipitations has not been settled. This has been done in some cases and in others not, but the effect, if any, on the final yield of active material has, so far, not been established by physiological tests.

Both (I) and (II) are decomposed by suspending in about 25 cc. of water and passing a rapid stream of hydrogen sulfide through each mixture until the conversion of the silver to sulfide appears complete. The silver sulfide is conveniently separated by centrifugation and the clear supernatant liquid filtered. After volatilization of the excess of hydrogen sulfide by slight warming and subjection to diminished pressure, the solutions are each subjected to reprecipitation with the silver nitrate and ammoniacal silver nitrate reagents exactly as done in the first place.

Fraction (I) now yields a precipitate with silver nitrate and the supernatant liquid from this furnishes a considerable amount of precipitate on addition of ammoniacal silver nitrate. This is later added to the main portion of precipitate (II).

The original fraction (II) gives only an insignificant amount of precipitate with silver nitrate and the product now obtained with ammoniacal silver nitrate turns dark much more slowly than during the previous precipitation. Furthermore, after the precipitation with ammoniacal silver nitrate is brought to completion, the supernatant liquid may yield a further amount of curdy precipitate by addition of silver nitrate. This is particularly true for the third precipitation and it therefore appears that for complete silver precipitation a narrow adjustment of the proportions of the two reagents is required. In some cases the second and subsequent precipitations of (II) have been made by alternate additions of silver nitrate and ammoniacal silver nitrate solution. The final clear supernatant liquid obtained by centrifugation is always tested with both reagents before being rejected.

Both (I) and (II) should be washed one or more times by stirring with water and centrifuging and then spread on porous plates to dry. During the drying the precipitates contract in volume and (I) always turns dark brown or black in color. In the case of (II) the darkening is usually not so pronounced. After a third precipitation and sometimes after the second, (II) retains its white color during the drying, but no sample of (I) has so far been found to retain its original white color after being dried on the porous plate.

The ammoniacal silver nitrate precipitate (II) obtained from the first silver nitrate precipitate (I) is mixed with that obtained by reprecipitation of the first ammoniacal silver nitrate precipitate (II). This mixture is suspended in water and treated with hydrogen sulfide as was previously done. The clear filtrate from the silver sulfide, when freed of the excess of hydrogen sulfide, is precipitated as previously described, and ordinarily constitutes the final pure antineuritic product which has previously been designated as "silver vitamine compound." The average quantity of the dry white product obtained from 300 g. of "activated solid" is 2.5 g.

CHEMICAL NATURE OF THE SILVER PRECIPITATES

PRECIPITATE (I)—It is well known that many compounds, particularly purines, give curdy, insoluble precipitates with silver nitrate both in acid and alkaline solution. In the present case it has been found that the two or more times reprecipitated silver nitrate fraction (I) is mainly, if not entirely, a silver compound of adenine. The identification of this purine was made by decomposing the precipitate suspended in water, with hydrogen sulfide, and slowly evaporating the filtrate from the silver sulfide, to crystallization. The crystals which separate respond to the phenolsulfonic acid test for nitrate and yield an insoluble picrate which corresponds in all its properties to adenine picrate. The melting indications of the latter are unchanged when mixed with an approximately equal amount of authentic adenine picrate. The percentage of nitric acid in the crystals, as estimated by colorimetric comparison of the products of the phenolsulfonic acid reaction, corresponds closely with that required for adenine nitrate. The yield of adenine nitrate obtained in this way from 300 g. of activated fuller's earth was, in several cases, found to be about 0.5 g.

Since no nitric acid was added in the above experiment, it is evident that the amount required to form the crystalline adenine nitrate must have been derived from the silver adenine precipitate. In order to obtain information on this point, and also on the silver content of the precipitate, four samples prepared from different lots of vitamine extract were analyzed, by ignition, for silver, and by the colorimetric phenolsulfonic acid method, for nitrate. The following results were obtained:

SAMPLE No.	Per cent Ag	Per cent HNO_3
1	46.84	12.0
2	42.89	17.4
3	46.87	15.8
4	41.15	21.0

Sample 1 was a composite lot of six dried silver nitrate precipitates obtained by various slight modifications of the general method.

Sample 2 was obtained by precipitating three times and drying thoroughly after each precipitation.

Sample 3 was likewise dried after each of the three precipitations. It was obtained from a vitamine extract prepared from a sample of activated fuller's earth less active, physiologically, than that used for the preceding precipitates.

Sample 4 was prepared by precipitation of the mother liquor from adenine nitrate crystals obtained from a solution prepared by decomposition of the initial silver nitrate precipitate (I) by means of hydrogen sulfide.

These results, therefore, represent a considerable range of variation in the preparation of the silver nitrate precipitate (I). The constant presence of nitrate or nitric acid in these well-dried samples is noteworthy.

The results for per cent of silver agree in general with the accepted formula, $C_5H_4N_5Ag$ (= 44.4 per cent Ag), for adenine silver, but when the presence of the nitrate is taken into consideration the agreement is not so good. The fact that the nitrate is retained so persistently by this precipitate (I) and by the ammoniacal silver nitrate precipitate (II), as will be shown later, is believed to be of significance in explaining previous failures to isolate active crystalline material.

PRECIPITATE (II)—Turning now to the characteristics of the ammoniacal silver nitrate precipitate (II), it is found that a part, or in some cases all of it, may accompany the silver nitrate fraction, during the first precipitation of the crude vitamine extract. When, however, it has been separated completely from the latter by reprecipitation, it then does not yield a precipitate with silver nitrate in absence of ammonia. Fraction (II) rapidly redissolves in excess of the ammoniacal reagent or of ammonia. Furthermore, its reprecipitation is usually not complete with ammoniacal silver nitrate alone. The addition of silver nitrate after the end-point with ammoniacal silver nitrate yields in these cases a further considerable quantity of precipitate. Thus an alkalinity represented by less ammonia than required for complete re-solution of ammonia-precipitated silver hydroxide is necessary for maximum precipitation of (II). These characteristic differences between (I) and (II) show conclusively that some other compound than adenine is responsible for the properties of fraction (II), which the physiological tests, as previously reported, have shown to possess considerable antineuritic activity.

In regard to the composition of fraction (II), as shown by analysis, it is found that the silver content varies over a wide range but is much higher than found for the silver nitrate fraction (I). The content of nitrate (nitric acid) is, however, much lower. Results for seven samples are as follows:

SAMPLE No.	Per cent Ag	Per cent HNO_3
1	55.0	10.8
2	55.6	5.1
3	57.5	5.4
4	62.0	Not det.
5	49.4	6.7
6	46.0	4.3
7	51.5	6.8

Sample 1 was prepared by three precipitations, drying each thoroughly on a porous plate before proceeding to the next.

Sample 2 was precipitated from the mother liquor of the crystals obtained from Sample 1, by decomposition in the usual manner with hydrogen sulfide and slow evaporation of the filtrate from the silver sulfide. The yield from 3.68 g. of No. 1 was 0.46 g. of crystals, 0.57 g. of precipitate with ammoniacal silver nitrate, and 0.6 g. with silver nitrate. There was, consequently, considerable unaccounted loss.

Sample 3 was twice precipitated and dried on a porous plate after each precipitation.

Sample 4 was not dried on a porous plate after each precipitation, but was washed three or more times by stirring with somewhat more than an equal volume of water, centrifuging, and decanting the wash water.

Sample 5 was dried on a porous plate after each of three precipitations.

Sample 6 was obtained from the first silver nitrate precipitate and was not reprecipitated.

Sample 7 was prepared from "activated solid" which had begun to show evidences of molding and was of reduced vitamine activity. An exceptionally large amount of fraction (I) was obtained and none of fraction (II) at the first precipitation. The aqueous solution prepared by hydrogen sulfide decomposition of (I) was first subjected to crystallization and from the mother liquor, the present sample was obtained by the usual silver nitrate and ammoniacal silver nitrate precipitation.

As before, the silver was determined by ignition and the nitric acid by the phenolsulfonic acid colorimetric procedure. In this case, however, it was necessary to remove the silver from the alkaline solution before making the color comparisons. This was done by acidifying with hydrochloric acid, filtering, and restoring the color by adding excess of alkali.

A noteworthy point, in connection with these results, is that the percentage of silver was highest in Sample 4, in the preparation of which more washing was employed than in any other case. This would indicate that the precipitate is hydrolytically decomposed, with excessive removal of the more soluble organic constituent of the complex. This, taken in connection with the solubility of the precipitate in excess of ammonia, emphasizes strikingly the practical impossibility of controlling the conditions in a manner which might insure a product of constant composition.

Another point of interest is the constant presence of nitrate (or of nitric acid), even in samples which were repeatedly dried on a porous plate and by vacuum desiccation. It is regretted that Sample 4 was exhausted before the nitric acid determinations were made.

Experiments made with the object of separating in a pure condition the active compound united with silver in fraction (II) usually result as follows: The well-dried sample is suspended in water and hydrogen sulfide passed in to convert the silver to sulfide. The aqueous filtrate from this, when evaporated slowly, first yields a small amount of crystalline crusts which adhere to the sides of the dish above the surface of the evaporating liquid. By decanting at the proper time gradual crystallization may occur and large, well-formed, prismatic crystals slowly develop throughout the concentrated liquid. The exact conditions for the gradual crystallization are, however, difficult to realize, and usually the volume of liquid simply continues to diminish until it is a thick viscous mass. When it reaches this condition of supersaturation, stirring with a glass rod causes immediate crystallization, and the sirupy liquid is quickly transformed to a solid mass of minute crystals. The removal of a certain amount of the adhering mother liquor from this mass can be effected by spreading on a porous plate.

In one case in which the large crystals were obtained they were found to darken gradually and to melt with effervescence at about 205°. In the case of all the other samples, which were obtained by crystallization induced in a supersaturated solution and were dried on a porous plate, the melting point was found to be at approximately 178°.

The yield of the 205° crystals from 300 g. of "activated solid" was in the one case 0.46 g. The yields of the less pure 178° product obtained from the same amount of "activated solid" were 0.8, 1.02, 1.14, and 1.12 g., respectively. The 1.02 g. sample contained approximately 40 per cent of HNO_3, determined by the phenolsulfonic acid colorimetric method.

If the 178° crystals are dissolved in very little water and absolute alcohol is added, a point will be reached at which a white cloud separates. This gradually changes to minute needle-like crystals. The addition of ether appears to increase the yield of these fine crystals. When they are filtered off, washed with ether and dried, they melt quite sharply with only slight darkening and gas evolution at 214°.

These crystals dissolve instantaneously in water, and the solution gives no precipitate with aqueous silver nitrate alone but does when ammonia is added. Ammoniacal silver nitrate naturally gives an immediate curdy precipitate which redissolves in excess of the reagent or of ammonia. The aqueous solution of the crystals gives no precipitate with picric acid or sodium picrate. Likewise, no separation of an insoluble compound occurs upon addition of iodine solution or of mercuric chloride. A white precipitate is, however, obtained with phosphotungstic acid. An approximate determination of the nitric acid content of the crystals by the phenolsulfonic acid method gave 31.3 per cent.

From a consideration of the above properties, it appeared probable that the compound might be histidine nitrate. A positive test obtained on applying Pauly's reaction with *p*-diazobenzenesulfonate strengthened this view. The only nitrate of histidine mentioned in Abderhalden's "Biochemisches Handlexikon" is the dinitrate which contains 44.8 per cent HNO_3 and melts at 149° to 152°. Mononitrate would contain 28.9 per cent HNO_3. It was, therefore, decided to attempt to prepare histidine mononitrate and determine its melting point alone and when mixed with the present sample.

The mononitrate was prepared by mixing the calculated quantities of histidine and nitric acid and crystallizing from ether-alcohol. The resulting crystals melted at 232°. A mixture of about equal parts of this sample and the crystalline nitrate obtained from the ammoniacal silver nitrate fraction (II) began to soften below 150°, and complete liquefaction, with considerable effervescence, occurred some time before the temperature reached 200°. This appears to be satisfactory evidence that the unknown nitrate from fraction (II) cannot be histidine mononitrate.

Of the other known compounds which respond to the reaction with *p*-diazobenzenesulfonate, histamine (β-iminazolyl-ethylamine) corresponds very closely with histidine in many of the reactions. Tests were, therefore, sought to differentiate between the present sample and histamine. Of these the indications of the biuret reaction were inconclusive since an undoubted positive test could not be obtained with either a sample of authentic histidine or the unknown nitrate from the silver fraction (II).

It is stated that the dipicrate of histamine is very sparingly soluble in water. All attempts to obtain an insoluble precipitate on adding sodium picrate to a solution of the unknown nitrate were unsuccessful. It, therefore, appears improbable that the present crystals are a salt of histamine, but a final decision on this point requires further evidence.

In this connection, it should be mentioned that Dr. M. X. Sullivan of this laboratory states that he was able to identify histamine in vitamine fractions obtained by him several years ago, but he has, so far, not published his experiments.

Of the other compounds which respond to the Pauly *p*-diazobenzenesulfonate reaction, and correspond very closely in other respects with the nitrate here described, carnosine nitrate is stated to melt at 211° to 212°. Its content of nitric acid, however, as calculated from the accepted formula, is 21.8 per cent, therefore making it improbable that the present compound, containing 31.3 per cent HNO_3, can be carnosine nitrate.

Physiological Tests

Physiological tests of the various samples described in the previous pages were made by administering measured doses at regular intervals to pigeons given polished rice as their sole food. Under these conditions the vitamine content of the sample can be roughly estimated from the changes in weight of the pigeon, as compared with control pigeons receiving no added vitamine. In some instances curative tests were also made. In these cases the pigeons, receiving an insufficient amount or no vitamine, are allowed to proceed to initial but well-marked polyneuritic condition and then given doses of the sample in question. A prompt alleviation of the typical symptoms, followed by protection from recurrence of polyneuritis for several weeks, was taken as evidence of the curative and at least partly protective properties of the sample.

In general, control pigeons begin to lose weight promptly on a polished rice diet and decline to about 60 per cent of their original weight and develop typical polyneuritis within about 20 days. Occasionally, however, birds may decline at a slower rate and finally die after 40 to 60 days without showing any well-marked paralysis. A considerably larger number of such birds than ordinarily met have rendered some of the present results less definite than might be desired.

Previous experiments with the silver nitrate precipitate (I) had shown it to be inactive. In regard to the recent results with the ammoniacal silver nitrate precipitate (II), it was found that in all cases prompt and complete cures of polyneuritis resulted from doses of 0.004 g. of sample, and repeated similar doses, on alternate days, prevented recurrence of polyneuritic symptoms for as long as the experiment was continued, which was usually three or more weeks. In no case, however, did a marked increase in weight occur. Furthermore, administration on alternate days of 0.004 to 0.008 g. doses of the thoroughly dried precipitate (II), did not prevent loss in weight of normal birds, as is found to be the case when adequate doses of "activated solid" or of crude vitamine extract are given. In these cases the rate of loss was at first approximately the same as that of control birds, but after a few weeks the curves began to flatten and a distinct advantage, resulting from the samples, was noticeable. The fact that polyneuritic birds are so greatly benefited by the silver compound and that normal birds apparently utilize it very slightly is difficult to explain.

The experiments made with the various fractions obtained from the silver precipitates showed that none was the equal of the silver precipitate (II) in relieving polyneuritis and preventing its recurrence.

An explanation of the repeated failures to secure active material from the silver complex may be found in the constant presence of nitric acid in this product and the consequent presence of this acid in every solution from which crystals were obtained. The suggestion for this explanation was obtained from one of the early experiments in which a crystalline nitrate was intentionally prepared from the ammoniacal silver precipitate and, when subjected to tests on pigeons, found to be entirely devoid of any curative or protective properties. The fact that all of the other crystalline products were nitrates was not ascertained until after completion of the physiological tests.

Summary

Of the insoluble compounds obtained from concentrated vitamine extracts by successive precipitation with silver nitrate and ammoniacal silver nitrate, the first was found to consist principally of adenine silver and the second of a silver compound of a base closely related to histidine. Both precipitates tenaciously retain nitrate or nitric acid and this remains in the solution after removal of the silver, with the result that the crystals, which are obtained on slow evaporation, are in both cases nitrates.

Feeding tests of the several crystalline compounds on pigeons showed that they retain very little, if any, of the antineuritic properties of the ammoniacal silver precipitate. It is possible that the loss of activity may result from the constant presence of nitric acid in the solutions from which the crystals are obtained.

The Antiscorbutic Vitamine

By Alfred F. Hess

16 West 86th St., New York, N. Y.

Far less is known of the antiscorbutic vitamine[1] than of the antineuritic vitamine. We know that the antiscorbutic vitamine is water-soluble; indeed, it has been called the water-soluble C vitamine. It is also soluble in alcohol and in acetone. It is not adsorbed by the fuller's earth method introduced by Dr. Seidell; in fact, from a mixture containing both water-soluble B and C vitamines it can be separated by this means.

Little more is known from a purely chemical point of view. But that does not imply that considerable progress has not been made in the past few years in regard to this vitamine. Indeed, since the publication of the report of the British Research Committee, only three years ago, views have altered essentially in this regard. It was previously supposed, and brought forth in 1918 in this report, that this vitamine is destroyed by drying, by aging, by the canning process, and by heating. That had long since been the accepted view in regard to the factors which lead to the destruction of the antiscorbutic vitamine and bring about the development of scurvy. Recently our ideas in this respect have undergone important modifications. Without going into detail in regard to drying, it may be stated that experiments of Dr. Unger and the writer,[2] substantiated by others, have clearly shown that although most substances lose the vitamine in the course of drying, desiccation does not necessarily destroy this vitamine. For instance, milk may be dried to a powder and nevertheless retain the major part of its vitamine. This dried milk may even be aged and still retain this vitamine. *It may be canned and aged and dried and still retain its antiscorbutic vitamine* and be able to cure infantile scurvy. In the course of the desiccating process it is subjected to about 240° F., so that we may add, it also may be heated and nevertheless remain antiscorbutic. It is evident that there must be some other factor or factors involved in its destruction.

Reference should be made in passing to the importance of the reaction of the medium to the stability of this vitamine. It is known to most of you that if an antiscorbutic food is acid, it is much less apt to undergo destruction. For instance, this is the main reason why orange juice can retain its highly antiscorbutic potency in spite of having been boiled. It explains why the tomato is a very efficient antiscorbutic, even after it has been heated, canned, and allowed to age. In our experience tomatoes canned a year were found to have retained their full antiscorbutic value.

Clearly there must be some further explanation for the instability of the antiscorbutic vitamine; heat, to which its destruction has almost universally been attributed, cannot be the sole or even the preëminent factor. The clinical reports of experienced physicians also lead to this conclusion. For instance, children's specialists in France have reported that they have fed thousands of babies on hundreds of thousands of bottles of sterilized milk in the course of years, milk that had been heated to the boiling point and over and that throughout this long period they have never encountered a case of scurvy. Surely, such extensive reports covering a period of years cannot be passed over lightly.

Effect of Oxidation on Destruction of Vitamine

Some experiments carried out by the writer in conjunction with Dr. Unger showed that there is another factor, perhaps a more important factor than those mentioned, which leads to the destruction of this vitamine, namely, *oxidation*.[1] This action can be demonstrated in a very simple way. For instance, if a liter of milk is treated with a very small amount of hydrogen peroxide (4 cc. of a normal solution) and allowed to stand over night in an incubator at blood heat, the antiscorbutic vitamine is almost entirely destroyed. This is tested by the biological method; 80 cc. of milk per day per capita are fed to a series of guinea pigs. It is found that all these guinea pigs develop scurvy, whereas control guinea pigs receiving the same amount of milk to which peroxide has not been added remain free from signs or symptoms. Furthermore, the guinea pigs which develop scurvy on this oxygenated milk rapidly lose all symptoms of this disorder when a few cubic centimeters of orange juice are added to the dietary. In other words, the small amount of peroxide thoroughly destroyed the antiscorbutic content of the milk, destroyed it to the same extent as heating milk to 100° C. for an hour. The authors showed also that if orange juice is subjected to a stream of oxygen its antiscorbutic potency is likewise diminished, and that the same is true of milk. This destructive effect of oxidation has been substantiated by experiments carried out by Dutcher[2] in this country and by Zilva at the Lister Institute in London.[3] That antiscorbutic vitamine is sensitive to oxidation is of importance from a theoretical as well as from an industrial point of view. It explains, for instance, why some dried milk possesses the antiscorbutic property, whereas other dried milk is markedly lacking in this factor.

When we stated some years ago that experiments showed that dried milk may have antiscorbutic value, our conclusions met with skepticism. It is now recognized that the nature of the product depends upon the process of drying. If, in the course of drying, milk is subjected to oxygenation, as it is in the spraying process, it loses much or most of its antiscorbutic vitamine, whereas if it is dried on a drum and its particles not subjected to the air, it is found to retain the greater part of this vitamine. Condensed milk retains considerable of this factor, owing to the fact that the condensation process is conducted with very little access of air. This new conception of the role of oxidation harmonizes many views which heretofore appeared discordant. It explains how the French physicians were probably quite correct when they reported encountering practically no scurvy in the course of feeding sterilized milk to babies; we had paid no attention to the fact that the milk which they fed had been heated in and kept in hermetically sealed bottles.

This probably is the more precise explanation of what we have called "aging," a term which is descriptive but hardly scientific. The aging which destroys the antiscorbutic vitamine is oxygenation.

---

[1] For fuller information on this subject reference may be made to the following papers by the author: "The Role of Antiscorbutics in Our Dietary," *J. Am. Med. Assoc.*, **71** (1918), 941; "Newer Aspects of Some Nutritional Disorders," *Ibid.*, **76** (1921), 693.

[2] "The Scurvy of the Guinea Pigs. III—The Effect of Age, Heat, and Reaction of Antiscorbutic Foods," *J. Biol. Chem.*, **38** (1919), 293.

[1] "The Destructive Effect of Oxidation on Antiscorbutic Vitamine," *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 143.

[2] R. A. Dutcher, H. M. Harshaw and J. S. Hall, "Effect of Heat and Oxidation on Antiscorbutic Vitamine," *J. Biol. Chem.*, **47** (1921), 483.

[3] "The Influence of Aeration on the Stability of the Antiscorbutic Factor," *Lancet*, **1921** [I], 478.

CATALYSIS

Another factor in the destruction of antiscorbutic vitamine is catalysis. Its effect may be illustrated by citing the following experiment. If milk is pasteurized (145° F. for 0.5 hr.), heating half of it in a glass vessel, and the other half in a copper vessel for the same length of time, the milk heated in the copper vessel will be found to have lost considerable of its antiscorbutic vitamine. On feeding 80 cc. per capita of these two lots of milk to a series of guinea pigs, the animals receiving the milk pasteurized in the copper vessel will develop scurvy, whereas those receiving the milk which had been heated in the glass vessel will thrive and not develop this disorder. That the signs and symptoms are truly those of scurvy is proved by their prompt disappearance—in spite of continuing the same milk—if a few cubic centimeters of orange juice are given in addition. The milk heated in the copper vessel contained but three or four parts of copper per million—a very small amount.

This experiment has a practical application for, as is well known, milk in the process of pasteurization passes through copper pipes; it is true that these are lined, but the lining frequently becomes defective after a short period. Lined copper vessels are commonly used in the course of condensing and drying milk. It is, therefore, not astonishing that copper is found very frequently in small amounts of milk. In a British medical report, it was found eleven times in eighty-seven samples. It is impossible to state how important a factor catalysis is. But whatever may prove to be the scope of its application, an experiment of this nature shows the little suspected factors which may be introduced and which must be taken into consideration in relation to the destruction of this most delicate vitamine, and warns us that in the handling of food products containing vitamines we must consider the influence of every new industrial process.

Quite apart from the question of the destruction of the vitamines, the last few years have demonstrated that we should not consider foodstuffs as entities from the standpoint of their vitamine content. A food may be rich or poor in this factor according to attendant circumstances. For instance, carrots cannot be classed as containing a definite amount of antiscorbutic vitamine; if they are fresh they will contain much more than if they are old, or, again, if they have been plucked young, they will have far more than if they were tough and old. We must avoid cataloguing foods too rigidly. It is probably of aid to arrange them in categories and to assign them definite potencies, but we must remember that such a list possesses merely comparative and approximate value.

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

Some Factors Affecting the Stability and Inversion of Oil-Water Emulsions[1,2]

By Leon W. Parsons and O. G. Wilson, Jr.

RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

SCOPE OF INVESTIGATION

This work covers some preliminary results obtained in the course of a fundamental investigation of the properties and behavior of mineral oil-water emulsions. Exact information regarding the properties of commercial emulsions is difficult to obtain and classify accurately on account of the complexity of the factors involved. It is felt that by obtaining more complete information regarding the general principles which govern the behavior of emulsions in simple systems and then applying the information to a systematic study of more complicated emulsions, greater progress may be made than by starting at once with the study of a few complex emulsions which happen to be of commercial importance.

Much, though not all, of the work thus far undertaken has dealt with the inversion point of oil-water emulsions. By definition the inversion point is that point where there is a change from an oil-in-water type of emulsion to a water-in-oil, or *vice versa*. This evidently marks a region of instability, and hence is of practical importance from the standpoint of breaking emulsions.

In general the work has been divided into three phases: (1) an investigation of the factors affecting the inversion point in the case of emulsions with water of a highly purified oil like Nujol; (2) in emulsions containing Nujol to which substances which are known to be present in commercial oils have been added; and (3) in the case of emulsions of different commercial oils. From such investigations, it is hoped that much fundamental information may be obtained which should be of assistance in solving the difficult problems involved in breaking commercial emulsions.

SOME GENERAL PROPERTIES OF OIL-WATER EMULSIONS

Although there is much information in the literature regarding emulsions, correlation of the results of various investigations is difficult on account of the difference in the nature of the materials used, the method of studying the emulsions, and the complexity of the factors involved.

From a consideration of the literature and from scattered information obtained from various oil companies, an attempt has been made in the chart in Fig. 1 to enumerate some fundamental properties of importance in considering the stability of commercial emulsions. Referring to this chart it will be seen that a rough division may be made of systems ordinarily called emulsions, into mechanical suspensions and true emulsions, the former being characterized chiefly by a greater instability; the latter being characterized by extreme stability which is in general produced by the presence of an effective emulsifying agent. It is realized, however, that no sharp line of demarcation may be drawn between the two. This investigation deals only with true emulsions.

---

[1] Presented at the Symposium on Emulsification Problems in the Petroleum Industry before the Section of Petroleum Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 41 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

A division of true emulsions into the two types, namely, oil-in-water and water-in-oil, is made and a general classification of the emulsifying agents which tend to produce these types, together with the various methods of breaking the emulsions, is indicated. In general, the emulsifying agents which tend to produce an oil-in-water type are those which are either soluble in water, the external phase, or which are more readily wetted by water than by oil. Correspondingly, in the case of the water-in-oil type of emulsions, solubility or greater wetting of the oil phase by the emulsifying agent is the necessary prerequisite. The present generally accepted theory of the formation of emulsions postulates the presence of a stabilizing film around the particles of the dispersed phase which prevents their coalescing. Although the exact nature of this viscous film is not clearly known, it is evident, as stated by Bancroft,[1] that the type and properties of the emulsions depend largely on the nature of this viscous film. Some work in this Laboratory[2] indicates that this film possesses the properties of a plastic solid. If the emulsifying agent could be altered so that it was wetted more by the internal phase, the emulsion should invert. Clowes[3] supported this theory and was able to change an oil-in-water emulsion stabilized by sodium oleate to a water-in-oil type by the addition of a calcium salt which formed the oil-soluble soap which is insoluble in water. Clowes further stated that when the equivalent ratio of sodium to calcium was 4 : 1, the effects were balanced and neither kind of emulsion was formed. These results were obtained from a study of emulsions of olive oil[4] which, on account of its composition and the impurities present in it, undoubtedly behaves differently from mineral oils. Bhatnagar[5] found that the 4 : 1 ratio above mentioned was affected by the volume ratio of the two phases as well as by other ions and that it changed with different soaps. In previous work in this Laboratory no critical ratio was found when magnesium and sodium oleates were used as emulsifying agents in the case of emulsions with Nujol.

It has been said that the inversion of phases could be effected by increasing the amount of dispersed phase until a critical point was reached where the dispersed phase became the continuous one. This point was supposed to be near the 74 per cent stable emulsion as described by Ostwald.[6] Pickering's[7] highly concentrated emulsion disproved this theory to some extent. Inversion by increasing the amount of dispersed phase implies that the emulsifying agent could stabilize either form of emulsion, forming a protective film about the small particles of either phase. This obviously opposes the Bancroft theory of emulsification and would tend to contradict the theories of Bancroft and Clowes as to the specific tendency of emulsifying agents to form one or the other type of emulsion. According to this theory, the nature of the stabilized film would have to be changed in order to produce inversion and the only effect of increasing the ratio of the dispersed phase should be to break (not invert) the emulsion, or else to allow the excess of the disperse phase to form a separate, nonemulsified phase.

In various technical emulsions it is often difficult to determine the exact nature of the emulsifying agent. In order to control intelligently the breaking of these emulsions, it is necessary first to determine the characteristics of the emulsifying agent, then to destroy it or convert it to an ineffective form.

As indicated in Fig. 1, there are several general physical methods of breaking which may be applied to both types of emulsion. In breaking emulsions by these methods the mechanism is undoubtedly due chiefly to a rupturing or destruction of the film by physical action—for example, by electrical treatment, change of temperature, distillation, etc.

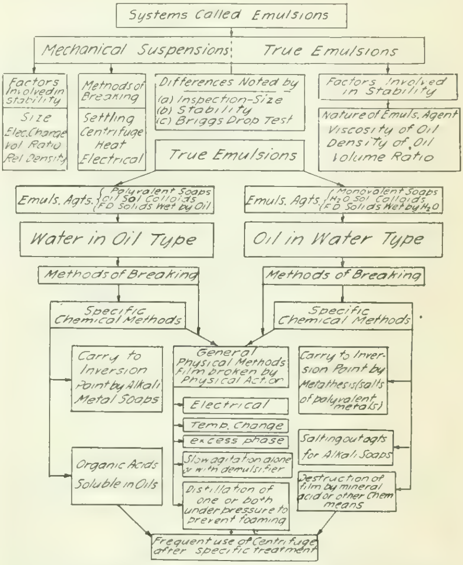

Systems Called Emulsions
Mechanical Suspensions
True Emulsions
Factors Involved in Stability
Size
Elec. Charge
Vol Ratio
Rel Density
Methods of Breaking
Settling
Centrifuge
Heat
Electrical
Differences Noted by
(a) Inspection-Size
(b) Stability
(c) Briggs Drop Test
Factors Involved in Stability
Nature of Emuls. Agent
Viscosity of Oil
Density of Oil
Volume Ratio
True Emulsions
Emuls. Agts. Polyvalent Soaps, Oil Sol Colloids, F D Solids Wet by Oil
Emuls. Agts. Monovalent Soaps, H2O Sol Colloids, F D Solids Wet by H2O
Water in Oil Type
Oil in Water Type
Methods of Breaking
Methods of Breaking
Specific Chemical Methods
Specific Chemical Methods
Carry to Inversion Point by Alkali Metal Soaps
General Physical Methods Film broken by Physical Action
Carry to Inversion Point by Metathesis (salts of polyvalent metals)
Electrical
Temp. Change
excess phase
Salting out agts for Alkali Soaps
Slow agitation alone or with demulsifier
Organic Acids Soluble in Oils
Distillation of one or both under pressure to prevent foaming
Destruction of film by mineral acid or other Chem means
Frequent use of Centrifuge after specific treatment

FIG 1—GENERAL PROPERTIES OF MINERAL OIL-WATER EMULSIONS

The specific chemical methods of breaking depend for their action either on carrying the emulsion to the inversion point or on destroying the film with specific chemical reagents. In order to invert an emulsion—for example, an oil-in-water type stabilized by sodium oleate—one must, in general, add a material which is soluble in water, the external phase, since by this means alone is it possible to penetrate readily the external phase, and affect the emulsifying film. In the above-mentioned emulsion this may be readily accomplished by the addition of calcium chloride which is water-soluble and which, by metathesis, produces calcium oleate which is soluble in oil. The addition of sulfuric acid or ether is an example of a specific chemical method of destroying the film.

PREPARATION OF EMULSIONS AND METHODS OF TESTING

For the larger part of the work Nujol was selected as the oil to be emulsified. This selection was made because Nujol, although essentially a medicinal oil, has been subjected to an extremely careful process of purification similar to that given other mineral oils, and from previous work in this Laboratory has been found fairly satisfactory for experimental comparison with commercial mineral oils, especially when impurities present in or extracted from these oils have been added to it. The Nujol used was found to give practically no coloration with sulfuric acid, and also showed no tendency to give stable emulsions with water alone. Aqueous solutions of sodium oleate were used as emulsifying agents for producing the oil-in-water type of emulsion. Magnesium oleate dissolved in Nujol was typical of an oil-soluble polyvalent soap which tends to give a water-in-oil type of emulsion.

---

[1] *J. Phys. Chem.*, **19** (1915), 275.

[2] *Chem. Met. Eng.*, **24** (1921), 19, 825.

[3] *J. Phys. Chem.*, **20** (1916), 407.

[4] *Ibid.*

[5] *J. Chem. Soc.*, **117** (1920), 542; **118** (1921), 61.

[6] *Z. Kolloidchem.*, **6** (1910), 103.

[7] *Koll. Z.*, **7** (1910), 11.

In preparing the emulsions the Briggs homogenizer[1] was used, with a capillary of about 1 mm. in diameter. All emulsions were prepared by first stirring vigorously for 2 min. by means of an electric stirrer and then passing the emulsion five times through the homogenizer. Microscopic examination showed that this procedure gave a uniform and fine-grained emulsion. From previous work in this Laboratory, it was decided to use equal amounts of oil and water in the majority of cases in order to keep the volume ratio of phases constant.

In studying the effect of various addition agents on emulsions, two methods were adopted. Material was either added to the separate components of the emulsion before mixing them, or added after the emulsion had already been made by the homogenizer treatment. It was thus possible to study the effect of addition agents both before and after the emulsion was formed.

Several methods were used to determine which was the external phase in the emulsions. The most satisfactory was the Briggs drop method,[2] which consists in touching a drop of emulsion to an excess of either pure phase. If the emulsion mixes readily the external phase of the emulsion is the same as the pure liquid used. Robertson's dye method,[3] in which the spreading of an oil-soluble dye into the external phase is tested, was also found useful. In general, a combination of these two methods, together with microscopic examination, gave satisfactory data regarding the character of the emulsions produced, although the drop method alone was in general quite satisfactory.

INFLUENCE OF VOLUME RATIO

Experiments were conducted to determine the effect of volume ratio on the stability of emulsions of Nujol and two commercial lubricants, and also to determine whether it was possible to invert an emulsion merely by varying the volume ratio.

The emulsions were prepared by adding 3 cc. of 0.033 *M* sodium oleate solution in different amounts of distilled water to the oils, varying the ratio of volumes of oil and water but keeping the total volume at 50 cc.

A maximum ratio of volume of oil to total volume of emulsion was found which gave a homogeneous oil-in-water emulsion. Above this value, which was 0.84 for Nujol and 0.83 and 0.87 for the other lubricants tested, a more fluid mixture was obtained which, on testing by the drop method immediately after mixing, appeared to be a water-in-oil emulsion. The mixture usually settled to three layers. The top layer contained some water dispersed in oil, but the drops were large enough to be visible to the naked eye, indicating a mechanical suspension rather than a true emulsion. The second layer was always too thin for satisfactory testing but appeared similar to the oil-in-water emulsions which resulted when the volume ratio was below the critical value. The lower layer consisted of excess water. After standing for some time the drops of water frequently settled out of most of the upper oil phase, leaving a clear layer of oil at the top.

It will be noted that the above critical values are all somewhat higher than the 74 per cent which represents the amount of interior phase which is possible with close packed spheres. The amount of excess emulsified above 74 per cent is therefore more or less of a measure of the ability of the films to resist rupturing when further and further distorted from their normal spherical shape.

In general, therefore, no true inversion point was noticed when the volume ratio alone was varied in the case of the three oils studied, but, as would be expected, there was a maximum amount of oil which could be emulsified by sodium oleate. Above this point, which was well defined for each oil, breaking occurred. This contradicts certain of the above-mentioned experimenters, but confirms the conclusions of Bancroft and Clowes. In order to eliminate the effect of volume ratio in subsequent experiments, the ratio of oil to total volume of emulsion was kept constant at 0.5, thus choosing a region in which the oil-in-water emulsions of Nujol would be fairly stable.

OPPOSING EMULSIFYING AGENTS IN DIFFERENT PHASES

An interesting series of emulsions was studied in order to determine the effect of opposing emulsifying agents, such as sodium oleate and magnesium oleate, which tend to produce oil-in-water and water-in-oil emulsions, respectively. The general method of experimentation was to shake a solution of sodium oleate in water with a solution of magnesium oleate in Nujol, keeping the volume ratio 50 : 50. A large number of emulsions were studied, varying the ratio of equivalent concentration of magnesium oleate to sodium oleate from 25 to 0.54. It was desired to obtain the characteristics of the above system when both emulsifying agents were present, in order to determine whether a real equilibrium existed and whether there was some critical ratio of the emulsifying agents at which point no emulsion at all would be formed.

In all cases the resulting emulsions settled out in three layers, oil on top, water on the bottom, and varying amounts of emulsion between. This middle emulsion layer was tested at different levels by withdrawing a portion by means of a capillary pipet and applying the drop test. In many cases both types of emulsion were found, water-in-oil in the upper portion and oil-in-water in the lower portion. After standing for several days a distinct line of demarcation was noticed in this emulsion layer, above which the drop test indicated the presence of a water-in-oil and below an oil-in-water emulsion.

This phenomenon was noticed in six emulsions in the series studied, where the ratio of magnesium oleate to sodium oleate varied from 1.0 to 10, and is now being very carefully investigated. It appears that an equilibrium is set up between the two types of emulsions and that, on standing, the less stable water-in-oil emulsion, which is much coarser grained than the oil-in-water, apparently undergoes gradual breaking, with the separation of oil. In the above experiments the systems were prepared in several different ways. In some cases an oil-in-water emulsion was made and then treated with magnesium oleate; in others, the water-in-oil was prepared and treated with sodium oleate; in others, a solution of sodium oleate in water and of magnesium oleate in oil were mixed simultaneously, all of the above series being put through the homogenizer. The presence of both types of emulsion was independent of the method of preparation.

Although the above series is being subjected to more critical investigation on account of the interesting characteristics observed, it appears that no ratio of magnesium oleate to sodium oleate was found where the opposing forces were balanced, giving an inversion point with no stable emulsion, but rather that some form of pseudo-equilibrium was set up whereby *both* types of emulsion were produced.

INVERSION BY METATHESIS

A study was made of the effect of aqueous solutions of various divalent and trivalent salts on the stability and tendency to invert of oil-in-water emulsions of Nujol. The oil-in-water emulsions were made in the usual way by stirring and homogenizing, using sodium oleate as the emulsifying agent. Aqueous solutions of magnesium sulfate, magnesium chloride, and ferrous sulfate were added in varying concentration as typical representatives of bivalent salts, and aluminium sulfate and ferric chloride in aqueous solution were the addition agents typical of the trivalent salts. The volume ratio of oil to total emulsion in the resulting mixture was 0.5 in each case.

---

[1] *J. Phys. Chem.*, **19** (1915), 223.

[2] Newman, *Ibid.*, **18** (1914), 34.

[3] *Kolloid. Z.*, **7** (1910), 7.

MAGNESIUM SALTS—It was found that if the equivalent concentration of magnesium was greater than that of sodium a complete inversion to the water-in-oil type resulted. In cases where the amount of magnesium salt was not sufficient to react with all of the sodium oleate, both types of emulsions were formed. The general appearance and properties of the latter emulsions were similar to those of the emulsions described above in the series on opposing emulsifying agents. In order to show definitely that the determining factor was the ratio of equivalents of magnesium to sodium rather than the absolute concentration of these substances, several runs were made in which the absolute concentration of magnesium salt was lower than that which had failed to invert completely in previous cases, reducing the sodium until it also was less than the magnesium. A complete inversion of the emulsion resulted, indicating the ratio to be the determining factor rather than the absolute concentration of magnesium sulfate added. Comparison of Emulsions 53 and 66 in Table I indicate the results above described.

The effect of using magnesium chloride was very similar to that of the magnesium sulfate and no indication was obtained of any appreciable variation in the inversion point due to a variation in the anion of the magnesium salt.

TABLE I—INVERSION BY METATHESIS

System—Sodium oleate in water, Nujol and $MgSO_4$ in water
$MgSO_4$ = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. $MgSO_4$ = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
50	Added	0.5	0.0279	0.32	11.5	Oil	Complete inversion
51	Added	0.5	0.0293	0.24	8.2	Oil	Complete inversion
52	Added	0.5	0.0306	0.16	5.2	Oil	Complete inversion
53	Added	0.5	0.0319	0.08	2.5	Oil	Complete inversion
54	Added	0.5	0.0266	0.04	1.5	Oil	Complete inversion
71	Added	0.5	0.0266	0.0266	1.0	Both	Very indistinct layers
55	Added	0.5	0.0293	0.024	0.82	Both	Partial inversion
56	Added	0.5	0.0306	0.016	0.52	Both	Partial inversion
66[1]	Added	0.5	0.0064	0.016	2.5	Oil	Complete inversion

[1] Shows that ratio of equivalents was the determining factor rather than absolute concentration.

TABLE II—INVERSION BY METATHESIS

System—Sodium oleate in water, Nujol and $MgCl_2$ in water
$MgCl_2$ = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. $MgCl_2$ = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
65	Added	0.5	0.0253	0.48	19.0	Oil	Complete inversion
64	Added	0.5	0.0279	0.32	11.5	Oil	Complete inversion
63	Added	0.5	0.0306	0.16	5.2	Oil	Complete inversion
62	Added	0.5	0.0266	0.04	1.5	Oil	Complete inversion
72[1]	Added	0.5	0.0266	0.0266	1.0	Oil	Complete inversion
61	Added	0.5	0.0306	0.016	0.52	Both	Partial inversion
60	Added	0.5	0.0319	0.008	0.25	Both	Partial inversion

[1] Compare with (71) in the preceding table. See discussion of metathesis.

The behavior of the solution during inversion was very interesting. When magnesium salt was added to an oil-in-water emulsion the viscosity was very greatly lowered while the salt was being added. Then the mixture became more viscous than the original emulsion, with oil appearing to be the external phase. It is possible that the magnesium first reacted with the sodium soap in the film and caused a temporary breaking of the emulsion, since the two phases formed a mixture possessing none of the high viscosity ordinarily characteristic of emulsions. The magnesium oleate formed by metathesis was then dissolved by the oil and on solution in the oil tended to disperse the water, giving a high viscosity characteristic of a true emulsion.

It should be noted that in the above cases no really sharp inversion point was obtained, but rather the presence of an unstable period of time during which inversion occurred.

FERROUS SULFATE—Since ferrous sulfate has been suggested as a demulsifier,[1] the effect of adding a solution of this salt to Nujol oil-in-water emulsions was investigated. In every case where the ratio of the equivalent concentration of ferrous sulfate to sodium oleate was above 1 an inversion was effected followed by a distinct breaking of the emulsion. This is essentially due to the weak emulsifying tendency of the iron soap produced by metathesis.

ALUMINIUM SULFATE—Aluminium sulfate in water was used as the inverting agent typical of a trivalent salt. The same phenomena as those indicated above were observed with regard to viscosity changes. Undoubtedly the effects produced were similar to those when magnesium salts were added, although the final result was modified somewhat by the extreme instability of the water-in-oil emulsions produced by the aluminium soap. Immediate breaking occurred to a certain extent, and the liberated water gave the effect of being the external phase when tested by the drop method before the emulsion had settled in layers. Complete inversion probably resulted when the concentration of aluminium sulfate was sufficient, but it was followed so quickly by breaking that the latter effect was the major one as indicated by the usual methods of testing.

In one case where the concentration of aluminium salt was not sufficient to react completely with the sodium oleate, the emulsion formed in two distinct layers. The upper one was a water-in-oil emulsion which was completely broken in 3 or 4 days, while the lower, in which water was the external phase, remained dense and unchanged for some time. At any concentration of addition agent the instability of these emulsions was an important factor although breaking must have occurred after inversion.

FERRIC CHLORIDE—Ferric chloride in aqueous solution also gave complete inversion of oil-in-water emulsions of Nujol but did not always produce breaking. An emulsion containing a ratio of equivalent concentration of ferric chloride to sodium oleate of 7.52 did not break for 24 hrs., and one whose ratio was 1.21 remained one of the most stable water-in-oil emulsions studied.

CONCLUSIONS—Fig. 2 shows a graphical summary of the results above indicated. In general the following conclusions may be drawn regarding the inversion of oil-in-water emulsions of Nujol by means of metathesis:

1—Divalent or trivalent salt dissolved in water could completely invert oil-in-water emulsions.

2—In the limited range studied, namely, in the case of magnesium chloride and magnesium sulfate, there is apparently very little effect due to a variation in the anion of the added salt.

3—In inversion by metathesis the ratio of equivalents of the inverting agent to the emulsifying agent was the determining factor rather than the absolute concentration of the former.

4—When the equivalent concentration of the polyvalent salt exceeded the monovalent, complete inversion took place. When it was less than the monovalent, a pseudo-equilibrium was established whereby some of both types of emulsion was produced.

5—The mechanism of the above inversion indicated first a chemical reaction destroying the film, then breaking the emulsion and forming the polyvalent soap, and finally solution of the polyvalent soap in the oil and emulsification with the phases inverted.

6—In general, sodium oleate, a monovalent soap, produced more stable emulsions than the polyvalent soaps in the case of Nujol systems. Of the polyvalent soaps studied magnesium oleate apparently gave the greatest stability.

SALTING OUT OF EMULSIONS

A brief study of the so-called "salting out" of emulsions was made in the case of oil-in-water emulsions of Nujol where

---

[1] U. S. Patent 1,093,098.

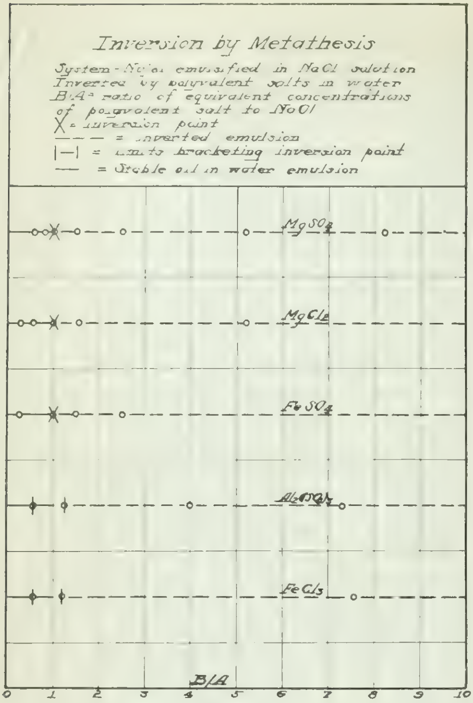


FIG. 2

sodium oleate was the emulsifying agent. Sodium chloride, iodide and sulfate were added in varying concentrations keeping the volume ratio always 0.5. One series was also studied where sodium chloride was added to a water-in-oil emulsion of Nujol produced by magnesium oleate.

TABLE III—SALTING OUT EMULSIONS—SODIUM CHLORIDE

System—Sodium oleate in water, Nujol and NaCl in water
NaCl in water = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. NaCl = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
35	Added	0.5	0.0173	0.48	27.7	None	Broke immediately
36	Added	0.5	0.0200	0.40	20.0	None	Broke immediately
37[1]	Added	0.5	0.0240	0.28	11.7	None	Broke immediately
44	Added	0.5	0.0253	0.24	9.1	None	Broke immediately
48	At once	0.5	0.0253	0.24	9.1	None	Broke immediately
45	Added	0.5	0.0259	0.22	8.5	None	Broke after some time
49	At once	0.5	0.0259	0.22	8.5	None	Broke after some time
38	Added	0.5	0.0266	0.20	7.5	Water	Creamed to two layers
47	At once	0.5	0.0266	0.20	7.5	Water	Creamed to two layers
39	Added	0.5	0.0280	0.16	5.7	Water	Creamed to two layers
46[1]	Added	0.5	0.0120	0.14	11.7	Water	Creamed to two layers
40	Added	0.5	0.0293	0.12	4.1	Water	Creamed to two layers
41	Added	0.5	0.0307	0.08	2.5	Water	Creamed to two layers
42	Added	0.5	0.0320	0.04	1.25	Water	Creamed to two layers
43	Added	0.5	0.0333	0	0	Water	Creamed to two layers

[1] Shows that conc. B determines salting out effect: compare Nos. 37 and 46.

The experimental results may be seen by reference to Tables III, IV, and V. Sodium chloride solution above a definite concentration broke the emulsions almost completely, but no indication of inversion was found. A concentration of 0.24 *M* sodium chloride was sufficient to break the emulsions immediately and a 0.22 *M* had the same effect after a few days. Below this value perfectly stable emulsions were produced. By comparing Emulsions 46 and 37 in Table III the effect of absolute concentration and ratio of concentration of emulsifying agent to addition agent may be seen. It was not possible to break the emulsion in (46) by decreasing the concentration of both sodium chloride and sodium oleate and still keeping a high ratio of chloride to oleate. This indicates that the absolute concentration of sodium chloride is the determining factor in breaking these emulsions.

TABLE IV—SALTING OUT EMULSIONS—SODIUM IODIDE

System—Sodium oleate in water, Nujol and NaI in water
NaI = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. NaI = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
120	Added	0.5	0.0240	0.28	11.7	None	Broke immediately
121	Added	0.5	0.0253	0.24	9.1	None	Broke immediately
122	Added	0.5	0.0259	0.22	8.5	None	Broke immediately
123	Added	0.5	0.0266	0.20	7.5	None	Broke immediately
125	Added	0.5	0.0273	0.18	6.6	None	Broke immediately
124	Added	0.5	0.0280	0.16	5.7	Water	Stable

TABLE V—SALTING OUT EMULSIONS—SODIUM SULFATE

System—Sodium oleate in water, Nujol and Na_2SO_4 in water
Na_2SO_4 = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. Na_2SO_4 = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
151	Added	0.5	0.0247	0.26	10.5	None	Broke immediately
150	Added	0.5	0.0253	0.24	9.1	None	Broke
152a	Added	0.5	0.0259	0.22	8.5	Water	Stable

Oil-in-water emulsions of Nujol were also broken by 0.18 *M* sodium iodide and 0.24 *M* sodium sulfate, indicating a slight variation, as near as experimental conditions could determine, in the minimum breaking concentrations due to a variation in the anion of the sodium salt used. The results obtained may be seen in Tables IV and V.

Indefinite results were obtained in investigating the salting-out effect of sodium chloride on water-in-oil emulsions of Nujol where magnesium oleate was the emulsifying agent. On account of the inherent instability of these emulsions breaking took place very easily and obscured the effect of the salt alone. It should be expected, however, that an aqueous solution of a salt would not give a well-defined reaction with water-in-oil emulsions on account of the inability of the salt in the aqueous phase to get at the emulsifying film, since in the case of water-in-oil emulsions the external phase is oil.

Generally speaking, to influence the properties of a particular film of emulsifying agent any substance which is added should be soluble in, or wetted by, the external phase of the emulsion in question. In this connection the following experiment is of interest.

A colloidal suspension of magnesium oleate in water was obtained by dissolving the oleate in acetone and adding the solution to a large quantity of water. On treating an oil-in-water emulsion of Nujol (sodium oleate as the emulsifying agent) with this colloidal suspension partial inversion took place with subsequent breaking of the emulsion. This was to be expected in view of the greater tendency of the magnesium oleate in colloidal suspension in one phase to dissolve in the other phase and exert its emulsifying action.

In general, from the above series of experiments on salting out, it was found that neutral monovalent salts, such as sodium chloride, iodide, and sulfate, gave no noticeable inverting action on oil-in-water emulsions of Nujol, but broke the emulsions by salting them out when the salt concentration was sufficiently high. The salting-out effect was a function of the concentration of salt added and not of the ratio of the concentration of salt to emulsifying agent.

In contrast to inversion by metathesis, the anion here appeared to have an appreciable effect, the minimum salting-out concentration being as follows: for sodium sulfate, 0.24; sodium chloride, 0.22; sodium iodide, 0.18.

In connection with future work on salting out of emulsions, it is planned to undertake a more thorough investigation of the mechanism of breaking emulsions by salting out with particular reference to the following points: The relation between the concentration of the salting-out substances and the concentration of emulsifying agent, a more complete study of the effect of various anions, a search for some oil-soluble "salting-out" agents, the general application of salting-out processes on a commercial scale, and a study of the development of the sodium chloride method for breaking emulsions as a laboratory tool for investigation.

EFFECT OF ADDITION AGENTS ON STABILITY OF EMULSIONS

As a second phase of the present investigation it was desired to ascertain the effect on the properties of oil-in-water emulsions of Nujol produced by sodium oleate of adding to these emulsions various substances known to be present in, or to exert an influence upon, emulsions met with in practice. The Nujol was emulsified in the usual manner with sodium oleate, and the stabilizing action of the added substance was measured by determining the concentration of sodium chloride solution necessary to break the emulsion. Although this sodium chloride treatment is rather an arbitrary test of stability, nevertheless it has been found to represent a fairly definite break point for other emulsions as well as Nujol. In every case the volume ratio was kept at 0.5 and the equivalent concentration of sodium chloride solution necessary to break the emulsion was recorded. The results are indicated in Fig. 3. Different methods were employed for adding the substances under investigation to the emulsions, varying according to the nature of the material used.

Since various sulfonates which are produced during the acid treatments of oils in the refining process exert a certain influence on the emulsifying tendencies of the oil, substances representative of this class of materials were added to Nujol, the resultant oil was emulsified, and the break point was determined by addition of sodium chloride solution. The substances used included pure sodium benzenesulfonate, the sodium salt of a sulfonated oil isolated from the acid treatment of a Texas oil, and the alcoholic extract from an acid-treated oil which in addition to containing various sulfonates contained certain amounts of sodium naphthenates. The sodium benzenesulfonate and the alcoholic extracts were added directly to the Nujol, whereas the sodium salt of the sulfonated oil was first dissolved in ether, then added to Nujol, and the ether evaporated. From Fig. 3 it is evident that the substances of this class have only a very slight effect, if any, on stabilizing oil-in-water emulsions of Nujol, as evidenced by the slightly higher equivalent concentration of sodium chloride necessary to break the emulsion.

Colloidal coloring matter obtained from a heavy lubricating oil was dissolved in ether and added to Nujol, and after removal of the ether by evaporation, the emulsifying tendency of the resultant mixture was determined. The sodium chloride necessary to break this emulsion was 0.24 *M*, practically the same as that required for the emulsion of Nujol alone. This indicates practically no effect of the colloidal coloring matter on the stability of the emulsion, at least as determined by the salting-out action of sodium chloride.

Since previous work in this Laboratory has indicated that amylene gives somewhat analogous results to other unsaturated bodies which are present in oils, the stabilizing action of amylene when added in various amounts of oil-in-water emulsions of Nujol was investigated. From Fig. 3 it is evident that the equivalent concentration of sodium chloride necessary to break these emulsions was much higher than when other substances were added to the Nujol. This indicates a marked stabilizing action on oil-in-water emulsions of Nujol by amylene, and it is interesting to note that the points thus determined fall on a fairly smooth curve. The significance of this curve, however, has not yet been clearly established, but is being subjected to further investigation. Although amylene and water give a rather unstable emulsion, the tendency of the amylene is toward stabilizing an emulsion of the oil-in-water type.

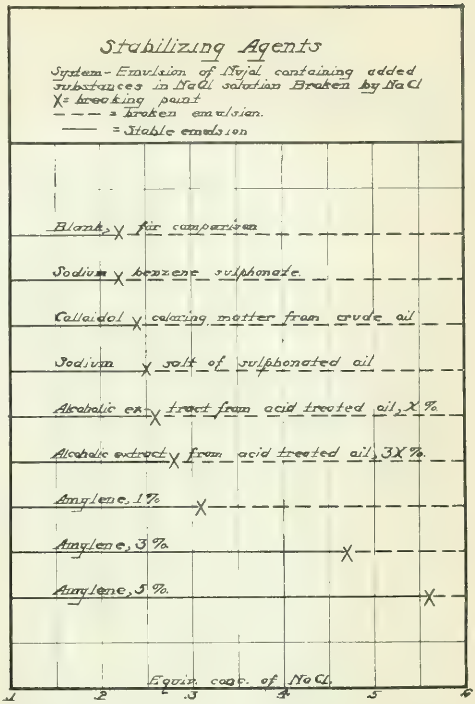


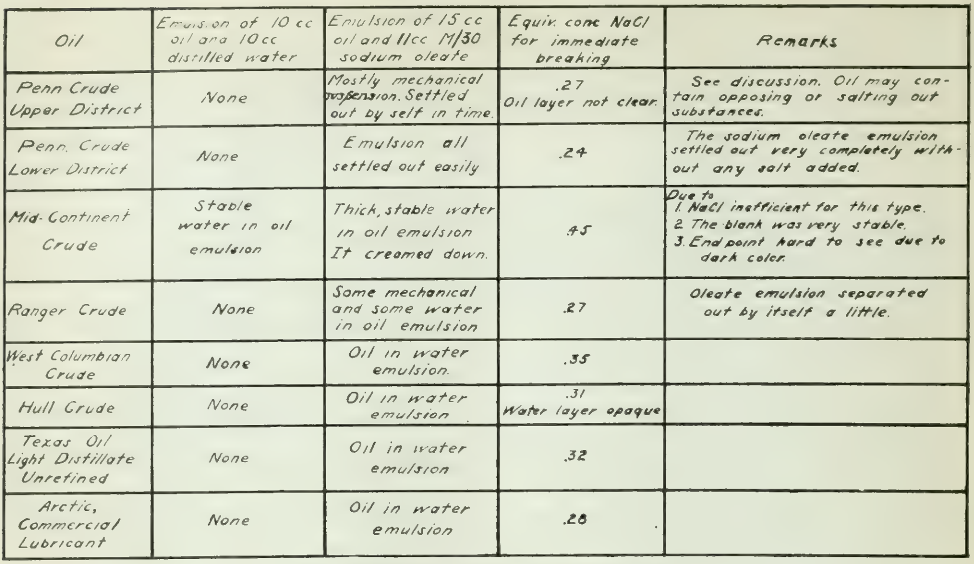
FIG. 3

In general, as indicated in Fig. 3, amylene is the only substance which exerts an important stabilizing effect when added to oil-in-water emulsions of Nujol. Other substances known to be present in commercial oil exert a very slight, if any, stabilizing action. This stabilizing action is determined by means of the concentration of sodium chloride necessary to break the emulsion.

INVESTIGATION OF COMMERCIAL OIL EMULSIONS

Several crude oils and a commercial lubricant were emulsified with sodium oleate in order to determine the stability of the emulsions thus produced, and also the concentration of sodium chloride necessary for breaking them. These crude oils were received directly from the wells and contained all the impurities common to their respective localities, having been subjected to no refining process. The oils were first agitated with an equal volume of distilled water to discover any emulsifying action of the oil with water, and 15 cc. of the oil were then emulsified with 11 cc. of 0.033 *M* sodium oleate. Two samples were made of the latter. One was allowed to stand untreated and the other was salted out with sodium chloride. The results are indicated in Fig. 4.

In the emulsion of the Upper District Pennsylvania crude with sodium oleate, a very unstable system similar to a mechanical suspension was formed. This could be accounted for in two ways: either something present in the oil reacting with the sodium oleate to produce an emulsifying agent with



Oil	Emulsion of 10 cc oil and 10 cc distilled water	Emulsion of 15 cc oil and 11cc M/30 sodium oleate	Equiv. conc NaCl for immediate breaking	Remarks
Penn Crude Upper District	None	Mostly mechanical suspension. Settled out by self in time.	.27 Oil layer not clear.	See discussion. Oil may contain opposing or salting out substances.
Penn. Crude Lower District	None	Emulsion all settled out easily	.24	The sodium oleate emulsion settled out very completely without any salt added.
Mid-Continent Crude	Stable water in oil emulsion	Thick, stable water in oil emulsion It creamed down.	.45	Due to 1. NaCl inefficient for this type. 2. The blank was very stable. 3. End point hard to see due to dark color.
Ranger Crude	None	Some mechanical and some water in oil emulsion	.27	Oleate emulsion separated out by itself a little.
West Columbian Crude	None	Oil in water emulsion.	.35	
Hull Crude	None	Oil in water emulsion	.31 Water layer opaque	
Texas Oil Light Distillate Unrefined	None	Oil in water emulsion	.32	
Arctic, Commercial Lubricant	None	Oil in water emulsion	.28	

FIG 4—EXPERIMENTS ON CRUDE AND COMMERCIAL OILS

CONCLUSION:

The oils may be put in three groups: (1) those which tend to resist emulsification (both Penn. oils and Ranger); (2) those which disperse the water (Mid-Continent); (3) those which aid oil-in-water emulsification (all others listed).

a tendency toward the water-in-oil type, or else, the presence of some salting-out material in the oil, more probably the former. An emulsion of the same oil made with magnesium oleate gave a distinct water-in-oil type, but was broken more easily than the one made with sodium oleate. The oil therefore had no particularly strong tendency to become the external phase, but merely resisted emulsification of any type. A similar effect was noticed in the case of the Lower District Pennsylvania crude. In all cases the mixtures formed were very unstable, requiring a slightly lower concentration of sodium chloride to salt out than was true in the case of the Upper District oil.

It will be noticed in the case of the Mid-Continent crude that with water alone a water-in-oil emulsion is obtained, whereas when the oil is treated with sodium oleate there is still a tendency toward production of a water-in-oil type. This oil obviously contains some emulsifying agent tending to produce a fairly stable water-in-oil type and requiring a fairly high concentration of sodium chloride for breaking. A similar tendency toward a water-in-oil type was noted in the case of the Ranger crude when emulsified with sodium oleate.

The last four oils listed in the chart behaved very similar to Nujol. No emulsion was formed with water but a fairly stable oil-in-water emulsion was produced with sodium oleate and was easily broken by a moderate concentration of sodium chloride.

The above series of observations, although limited in scope, indicate some of the simplest characteristics of these oils when treated with sodium oleate and broken with sodium chloride. The exact mechanism and behavior of this sodium chloride treatment is being further investigated and the range of applicability of this method as a laboratory tool is being determined.

CONCLUSIONS

1—This investigation covers some preliminary results obtained in a study of the factors influencing the stability and inversion point, in emulsions of Nujol and water, and then in Nujol-water emulsions to which substances present in commercial oils have been added. A comparison of the properties of the above systems with different commercial oils is made. Although most of the results obtained relate specifically to emulsions of Nujol, some fundamental observations have been made which, when extended, should throw considerable light on the problems involved in the stability of commercial emulsions.

2—No true inversion point was noted when the only variable was the ratio of the volume of the two phases.

3—In studying the effect of opposing emulsifying agents by mixing solutions of sodium oleate in water with magnesium oleate in oil, no sharp inversion point was found, but a pseudo-equilibrium appeared to be established, some of both types of emulsion being indicated by the drop test. These emulsions were frequently separated by a sharp line of demarcation. This appears to be contradictory to some results in the literature, though the experiments were not strictly analogous.

4—The following divalent and trivalent salts in aqueous solution were able completely to invert oil-in-water emulsions of Nujol by metathesis: $MgSO_4$, $MgCl_2$, $FeSO_4$, $Al_2(SO_4)_3$, $FeCl_3$. In this metathesis the ratio of equivalents of metallic precipitating ions was the determining factor rather than their absolute concentration. When the equivalent concentration of polyvalent metal exceeded that of monovalent soap, complete inversion resulted. When it was less, there was partial inversion similar to that above described, both types of emulsions apparently being present. The probable mechanism of this metathetical inversion is discussed. Variation in the anions of the precipitating salts studied had no appreciable effect on the results.

5—Neutral monovalent salts such as sodium sulfate, sodium chloride, and sodium iodide had no inverting action on oil-in-water emulsions, but when present in sufficient concentration broke the emulsion, presumably by "salting out" the soap film. This salting-out effect was a function of the salt concentration, not of the ratio of concentrations of salt to soap. A variation in anion appeared to have some effect in inversion by salting out, the minimum salting-out concentration in equivalents being as follows: Sodium sulfate, 0.24; sodium chloride, 0.22; sodium iodide, 0.18.

6—A study of the effect of the addition of certain substances present in commercial oils indicated a very weak stabilizing effect on oil-in-water emulsions of Nujol. Amylene, however, stabilized these emulsions somewhat in proportion to its concentration.

7—A brief study was made of the emulsifying tendencies of some crude oils with water and with sodium oleate solution together with the concentration of sodium chloride necessary to break these emulsions.

The Dehydration of Tar in the Laboratory[1]

By **Wilbert J. Huff**

THE KOPPERS COMPANY LABORATORIES, MELLON INSTITUTE, PITTSBURGH, PA.

The condensing systems which remove most of the tar from gas generally chill this gas well below its dew point; consequently raw tar usually contains considerable water. Subsequently the water content is usually reduced to a few per cent by gravity separation but this separation is never complete and in the case of very viscous tars, such as certain coal tars and tars having a gravity close to that of water, such as certain water-gas tars, the gravity separation is very unsatisfactory and some tars retain a very high percentage of water after standing indefinitely. For this reason, tars are generally held to be emulsions. Any tar containing more than a few tenths of a per cent water, if heated rapidly, may foam or bump badly. Consequently the elimination of the water is an extremely important problem for the tar distiller and the chemist engaged in the examination of tars.

For the dehydration of tar and other organic emulsions, a large number of procedures have been proposed.[2] In general the laboratory methods involve distillation following the addition of a solvent, or surface evaporation. The removal of water by centrifuging or by electrostatic attraction is not complete, and these methods are, therefore, not generally used in the laboratory. Grinding with carbon black and centrifuging with a solvent permit the rapid estimation of water,[3] but present the disadvantage that the tar residue cannot conveniently be used for further study. Methods which involve the addition of a suitable solvent and distillation, such as for instance the excellent method of Dean and Stark,[4] do not permit the determination of the light oil on the same portion of the sample and are generally not used when the chief object is the complete examination of the distillates and pitch.

For such studies, resort is had to surface evaporation processes which involve heating the tar from above, usually with a ring burner.[5,6] These methods, however, present the disadvantage that the heat is generally not confined to the upper portions of the tar; consequently many tars froth and spatter disastrously in spite of the most exacting care on the part of the operator. A current of gas[7] is sometimes passed through the tar to overcome this disadvantage; but this expedient is not ideal, because the gas current, unless chilled to low temperatures, will carry away uncondensed vapors of water and light oils. Moreover, the mechanical stirring action of the gas stream carries the heat to the lower portions of the still charge, thus assisting in superheating and the attendant dangers unless the entire operation is carefully watched.

Another expedient involves the slow addition of the tar to the still containing a small quantity of hot dehydrated tar. This is successful with very troublesome tars, but requires attention and special provisions for feeding.

To obviate these disadvantages, the writer has suggested a method now used in the laboratories of The Koppers Company. The tar is placed in the usual laboratory tar still, connected through the usual stillhead to the customary condenser and graduated receiver. Before closing the still, the position of the upper surface of the tar is marked. The lower portion of the still is then surrounded with a cylindrical receptacle open at the top—such as a pail—whose diameter is somewhat greater than the diameter of the still. This is so adjusted that the top of the receptacle is a little lower than the tar level. Water is added to the receptacle until it overflows. Heat is applied directly to the shallow layer of tar exposed above the water jacket, using the customary ring burner. This portion of the tar soon attains a temperature above the boiling point of water and the steam passes into the hot space above, where it cannot condense without passing out of the still. The water jacket absorbs heat which would otherwise be transmitted to the lower portions of the tar; consequently these are not heated above the steam point and no spattering or disastrous frothing can occur. The level of water falls gradually by evaporation, permitting the dehydrating zone to fall slowly. At any one time, the layer of *wet* tar heated sufficiently to cause steam formation is relatively shallow, consequently the steam has an opportunity to pass off quietly. When the water level has fallen below the bottom of the still, the tar is practically dehydrated. The receptacle for water is then removed, and the distillation is continued as usual.

The method is so simple that the writer finds it difficult to believe that it has not been used before, but if so, he is unaware of such use. It permits the approximate determination of light oil and water on the same portion of the sample, requires no new apparatus and practically no attention, handles efficiently very stiff tars and tars of high water content, and can be applied with advantage to the laboratory distillation of most tars.

In common with other surface evaporation methods which use direct flame heating, this may be subjected to the criticism that superheating of the vapor space may induce cracking. However, it presents the important advantage that the initial heating takes place at the tar level when the heat capacity of the tar assists in preventing the attainment of unduly high temperatures. The criticism can be eliminated by jacketing the upper portion of the still with material of high heat capacity. However, under the most unfavorable conditions the error introduced by such cracking is problematical, and it is generally disregarded.

---

[1] Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] It is beyond the scope of this article to list these. Most of the important references have been listed by Dean and Stark, THIS JOURNAL, **12** (1920), 486.

[3] Odell and Thiele, *Gas Record*, March 23, 1921, p. 30.

[4] *Loc. cit.*

[5] Senger, *J. Gasbel.*, **45** (1902), 841; also *J. Soc. Chem. Ind.*, **21** (1902), 1475.

[6] Jayne, *J. Am. Chem. Soc.*, **25** (1903), 814.

[7] If gas is used, it should be inert. The practice of blowing air through tar should of course be avoided, for tar at elevated temperatures may absorb oxygen, and with some tars, the absorption of oxygen is accompanied with a marked diminution in the quantity of recoverable oils.

Benzenedisulfonic Acid from Benzenemonosulfonic Acid[1,2]

By C. E. Senseman

COLOR INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, WASHINGTON, D. C.

Of the several methods described in the literature for the preparation of benzenedisulfonic acid but few are specific in all details, such as concentration of acid, amount of acid, temperature, and time of heating. Barth and Senhofer[3] in 1875 described a method of sulfonating the monosulfonic acid by heating for 2 hrs. with an equal volume of fuming sulfuric acid. They neglected to record the strength of acid and proper temperature for carrying out the reaction. Koerner and Monselise[4] prepared the disulfonic acid by heating four volumes of an acid mixture, resulting from sulfonating benzene, 3 to 5 hrs. with three volumes of fuming sulfuric acid at 200° to 245°. Binschedler and Busch[5] described a method in which 24 kg. of benzene are added in a thin stream to 90 kg. of fuming sulfuric acid. The temperature is raised to the boiling point of benzene and continued for 2 to 3 hrs., during which time the mono-acid is formed. The temperature is then raised to 275° and continued for 20 min. Lambert's patent[6] specifies the heating of sodium benzene sulfonate with 1.5 times its weight of $NaH_3(SO_4)_2$ 2 to 3 hrs. at 200° to 240°. None of these investigators have reported either the yield of disulfonic acid or its ratio to the mono-acid.

In 1910 Polak[7] found that by heating 10 g. of barium benzenesulfonate with 24 cc. of 98 per cent acid at 209°, disulfonation was complete by the end of 4 hrs. The disulfonation was complete at the end of 3 hrs. when 10 g. of the barium monosulfonate were heated to 233° with 20 cc. of 12.5 per cent fuming acid.

EXPERIMENTAL

The benzenemonosulfonic acid used in this work is obtained in a crude form and purified by converting it into the barium salt by almost neutralizing with barium hydroxide and finishing off with an excess of barium carbonate.[8] After filtering, this solution is evaporated in steam evaporators and the drying completed in an electric oven at 190° for about 96 hrs. Thus prepared, the salt analyzes 99.9 per cent barium benzenemonosulfonate, the analysis being made by determining the barium present in 3 g. of the dried salt.

The apparatus used is an enameled kettle equipped with a metal bath and mechanical stirrer which has a speed of 36 revolutions per minute. An open peephole in the cover serves as an escape for steam and fumes, and also for inserting a thermometer into the sulfonating mass. About 0.5 hr. is required to bring the mixture to the desired temperature. This is not considered as a part of the total sulfonating period.

In order to determine the progress of the reaction, samples are removed in most cases at intervals of 1 hr. The sample is dissolved in water and neutralized with barium hydroxide and carbonate. From the amounts of soluble salts and barium found in an aliquot part of this solution the ratio of the disulfonic acid to the monosulfonic acid is found. In order to dry these salt mixtures completely it has been found necessary to dry them at a temperature of 190° for 72 hrs. Because of the indirect method of determining the disulfonic acid, inherent analytical errors may be responsible for differences of 1.5 per cent.

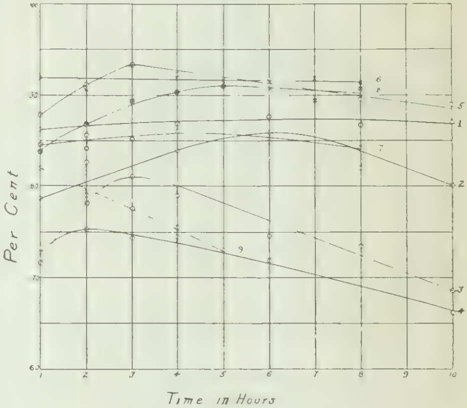


FIG. I

——— Temperature 250° C

------- Temperature 280° C.

1—95% acid, 300% excess 4—95% acid, 50% excess

2—95% acid, 150% excess 5—98% acid, 700% excess

3—95% acid, 50% excess 6—95% acid, 150% excess, catalyst Na

7—95% acid, 150% excess, catalyst V_2O_5

8—95% acid, 150% excess, catalyst Na and V_2O_5

9—95% acid, 150% excess

In Curve 1, Fig. I, are graphically represented the results obtained by heating 1.5 moles of the dried barium benzenemonosulfonate at an average temperature of 251° for 10 hrs. with 300 per cent excess of 95 per cent acid. With this concentration and excess of acid, sulfonation is practically complete at the end of 1 hr. Table 1 gives the analytical data for this and the following eight experiments. In this work the basis for calculating the per cent excess acid is that amount of acid actually required for the sulfonation, rather than the combined amounts that are required for the sulfonation and the precipitation of the barium.[1]

TABLE 1

	Av.	Acid			Yield of Disulfonic Acid in Per cent								
EXPT.	Temp. °C.	Per cent	Excess	Catalyst	1st Hr.	2nd Hr.	3rd Hr.	4th Hr.	5th Hr.	6th Hr.	7th Hr.	8th Hr.	10th Hr.
I	251	95	300	....	86.3	85.6	....	86.8	....	87.5	....	86.6	87.0
II	250	95	150	....	78.5	82.6	....	83.8	....	85.8	....	81.9	80.1
III	252	95	50	....	71.5	78.4	81.1	78.9	....	74.5	....	73.4	68.6
IV	251	98	50	....	72.7	75.3	74.3	74.5	....	71.8	....	....	66.1
V	250	95	700	....	87.8	91.1	93.3	92.2	....	90.3	....	89.5	88.9
VI	251	95	150	Na	91.9	90.5	....	91.8	91.4	91.3	91.8	91.2	....
VII	251	95	150	V_2O_5	84.5	84.1	85.2	86.0	....	84.8	....	84.2	....
VIII	252	95	150	Na and V_2O_5	84.0	86.7	89.3	90.2	90.9	....	89.3	90.7	....
IX	279	95	150	....	81.9	78.6	77.5	75.5	73.0	....	....	....	....

The effect of lowering the amount of excess acid to 150 per cent is shown by Curve 2, Fig. I. Ninety-five per cent acid was used and an average temperature of 250° was maintained for 10 hrs. It is seen that with this amount of excess acid 6 hrs. are required for the maximum production of the disulfonic acid. Further heating results in a loss of the desired product.

---

[1] Presented before the Section of Dye Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 17, 1920.

[2] Published as Contribution No. 52 of the Color Investigation Laboratory, Bureau of Chemistry, Washington, D. C.

[3] *Ber.*, **8** (1875), 1477.

[4] *Gaz. chim. ital.*, **6** (1876), 133.

[5] *Mon. Sci.*, **1878**, 1169.

[6] D. R. P. 113,784 (1899).

[7] *Rec. trav. chim.*, **29** (1910), 416.

[8] Because of the difficulty encountered in securing a sufficiently high-grade barium carbonate this reagent is prepared by treating a solution of barium hydroxide with carbon dioxide until precipitation is complete. The carbonate is then thoroughly washed.

[1] Attention is called to the fact that considerable barium sulfate is held in solution by sulfuric acid of this strength. However, its effect upon the rate of sulfonation has been shown by Polak (*Loc. cit.*) to be nil.

A further reduction in the amount of acid used gives the data for Curve 3, Fig. I, the excess acid used amounting to only 50 per cent. The acid concentration was the same as used in the two previous experiments. The average temperature for the 10 hrs. was 252°. The greatest yield of disulfonic acid was obtained after 3 hrs.' heating.

Curve 4, Fig. I, represents the results obtained when the monosulfonate is treated with 50 per cent excess of 98 per cent acid at an average temperature of 251° for 10 hrs. A slightly greater yield is obtained at the end of 1 hr. than when a 95 per cent acid is used. Further comparison is unfavorable to the 98 per cent acid, probably because the conditions are better for the carrying out of a secondary reaction which will be described later.

In obtaining the data for Curve 5, Fig. I, a much greater excess of acid has been used than for any other sulfonation, the excess amounting to 700 per cent. The acid concentration was the same as in Expts. I, II, and III, and the average temperature was 250°. The peak of the curve is reached in 3 hrs., after which time there is a slow falling off.

ADDITION OF CATALYSTS—Ambler and Cotton[1] found in their work on the sulfonation of benzene that sodium and vanadium pentoxide serve as catalysts. In Expt. VI, 0.1 per cent of the element sodium (calculated upon the weight of H_2SO_4 used) was added as Na_2CO_3. The total period of heating was 8 hrs., and an average temperature of 251° was maintained. The acid used was of 95 per cent concentration, in 150 per cent excess. Except for the addition of sodium all conditions were the same as in Expt. II. One hour's heating gave a yield of 91.9 per cent disulfonic acid, an increase of 13.4 per cent over that obtained at the end of the first hour in Expt. II. The entire Curve 6, Fig. I, is almost flat—the slight drop shown at the end of the second hour being due very likely to analytical errors.

Because of the presence of sodium in the sulfonating mass the analytical method had to be revised. After making the usual barium determination as the sulfate in a weighed quantity of the salts, sodium was determined as the sulfate by evaporating the solutions to dryness and ashing. From the weight of sodium thus found the barium equivalent was calculated, corrections made in the weight of the dried salts obtained, and the corresponding barium sulfate found.

The effect obtained by using vanadium pentoxide as a catalyst is shown in Curve 7, Fig. I. Five-hundredths per cent of the element vanadium (based upon the weight of H_2SO_4 used) was added as vanadium pentoxide. All other conditions remain the same as in Expt. VI. Again the curve obtained is almost a flat one, any one point being 6 to 7 per cent under that obtained in the previous experiment.

In Expt. VIII both sodium carbonate and vanadium pentoxide were used, 0.1 per cent of the former and 0.05 per cent of the latter. Except for an increase of 1° in the average temperature all other conditions were the same as in Expts. VI and VII. The yields throughout were below those obtained when sodium alone was used.

CHANGE OF TEMPERATURE—In Expt. IX a temperature change to 280° was made. One hundred and fifty per cent excess of 95 per cent acid was used. A comparison with Curve 2 shows that the higher temperature produces a greater amount of the acid in 1 hr., after which time there is a gradual falling off from 81.9 per cent to the 73 per cent resulting at the end of 5 hrs. At this temperature there is much charring of the materials.

SULFONATION AT 220°—In Fig. II are shown the curves which represent the results obtained by sulfonating at approximately 220°. Acid of 95 per cent concentration was used in each case, and the excess was 150 per cent. The analytical data for the four experiments are given in Table 2.

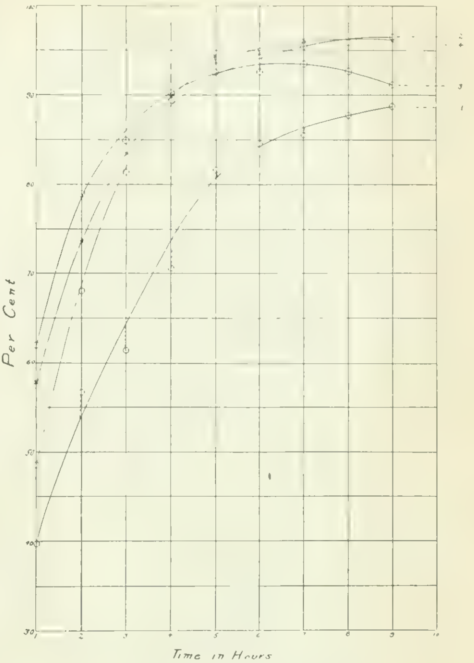


FIG. II

Temperature 220° C., 95% acid, 150% excess
1—Catalyst none 3—Catalyst V_2O_5
2—Catalyst Na 4—Catalyst Na and V_2O_5

TABLE 2

EXPT.	Average Temp. °C.	Catalyst	Yield of Disulfonic Acid in Per cent: 1st Hr.	2nd Hr.	3rd Hr.	4th Hr.	5th Hr.	6th Hr.	7th Hr.	8th Hr.	9th Hr.
I*a*	221	....	39.6	56.6	61.3	70.5	81.6	84.5	85.5	87.7	89.0
II*a*	220	Na	48.5	68.0	81.3	89.5	....	92.6	95.7	96.0	96.7
III*a*	221	V_2O_5	61.9	78.8	84.8	89.7	92.6	....	93.5	92.8	91.2
IV*a*	221	Na and V_2O_5	57.9	73.4	83.3	90.1	94.3	94.5	96.1	....	96.4

Expt. I*a*, employing no catalyst, was carried out at an average temperature of 221°. A fairly consistent increase in the production of the di-acid took place throughout the 9 hrs.' heating. At the end of the first hour 39.6 per cent was found, while 98 per cent was shown to be present at the completion of the 9-hr. period.

In Expt. II*a*, 0.1 per cent of the element sodium was added in the form of carbonate and an average temperature of 220° was maintained. Here again the benefit derived from the use of sodium is readily seen, inasmuch as the curve holds well above the preceding one. This curve reveals the largest yield of the di-acid of any so far recorded—96.7 per cent at the end of 9 hrs.' heating. The influence of V_2O_5 at a temperature of 221° is shown by Curve 3, Fig. II. The amount of the catalyst added was 0.05 per cent. In contrast to the experiments at higher temperatures, the yields obtained are greater for the first 5 hrs. than when sodium is used, after which time the production lags somewhat behind

---

[1] THIS JOURNAL, 12 (1920), 968.

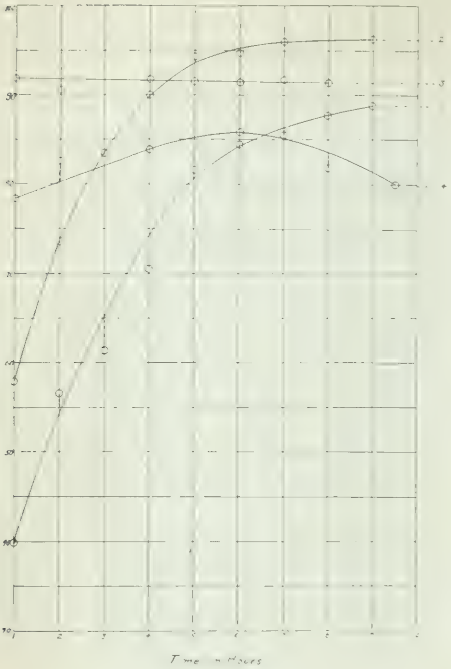


FIG. III

1—Temperature 220° C., catalyst none
2—Temperature 220° C., catalyst Na and V_2O_5
3—Temperature 250° C., catalyst Na
4—Temperature 250° C., catalyst none

that obtained with sodium. The results obtained by using both sodium and vanadium pentoxide at an average temperature of 221° are shown by Curve 4, Fig. II. Of the former 0.1 per cent was used, and of the latter 0.05 per cent was added. One hour's heating yielded 57.9 per cent of the diacid. Further heating gave a very consistent gain.

Curves 2 and 6, Fig. I, and 1 and 4, Fig. II, are brought together for a further comparison in Fig. III. These particular curves are chosen in order to represent clearly the best results with and without catalysts at both temperatures, 220° and 250°.

There is quite a noticeable drop in the amount of disulfonic acid found toward the end of some of the experiments. This is particularly true in those cases where the amount of excess acid is small, or a relatively high temperature is maintained, as shown by Curves 3, 4, and 9, Fig. I. This drop is probably due to the formation of sulfone compounds, such as benzenesulfonesulfonic acid, $C_6H_5SO_2C_6H_4SO_3H$, and benzenesulfonedisulfonic acid, $HSO_3C_6H_4SO_2C_6H_4SO_3H$.

The analytical results obtained where such compounds are present are, of course, in error in proportion to the amount of the sulfonesulfonic acid present. However, the actual amount of the disulfonic acid present is greater than the figures in such cases indicate. Evidence tending to prove the presence of such compounds was obtained by making sulfur determinations with the Parr calorimeter. More sulfur was found by this method than the barium method of analysis indicated was present.

Indication that a slightly greater amount of disulfonic acid is present at such stage in the sulfonation than the previous analytical results show is further given by fusion experiments made upon the purified sodium salts by Mr. Max Phillips of this laboratory. The methods of fusion and resorcinol determinations have already been described.[1] The optimum fusion conditions were followed. From the amount of resorcinol found in the fusion mixture the amount of disulfonate necessary for such a yield was calculated. This calculated amount was slightly greater than that found by determining the barium in a weighed sample of the dried salts.

SUMMARY

The sulfonation of benzenemonosulfonic acid was carried out at temperatures approximating 220°, 250°, and 280°, using acid of 95 and 98 per cent concentration and varying in quantity from 50 to 700 per cent excess. The time variation was from 1 to 10 hrs.

The results obtained show that:

1—Of the temperatures tested, 250° is the most efficient, considering time and quantity of acid used.

2—Ninety-five per cent acid gives better results than 98 per cent.

3—A large excess of acid, such as 300 to 700 per cent, is unnecessary.

4—Sodium (introduced as the carbonate) and vanadium pentoxide act as catalyzers separately, but no particular advantage is gained by using both.

5—With sodium as a catalyst, heating for 1 hr. is sufficient.

American Field Service Fellowships for French Universities

Attention is again called to the fellowships offered by the Society for American Field Service Fellowships for French Universities. Applications for the 1922–23 awards must be made not later than January 1, 1922.

These fellowships, not to exceed twenty-five in number, are of the value of $200 and 10,000 francs. They are awarded for one year, and may be renewed for a second year. They are offered in various fields of science, art, and literature.

Applicants must be citizens of the United States, between twenty and thirty years of age, and must be graduates of a college requiring four years of study for a degree or of a professional school requiring three years of study for a degree, or, if not qualified in either of these ways, must be twenty-four years of age and have spent five years in an industrial establishment in work requiring technical skill. A practical knowledge of French is also essential.

Application blanks and complete information regarding the fellowships may be obtained from the Secretary, Dr. I. L. Kandel, 522 Fifth Ave., New York City.

Perkin Medal Award

The Perkin medalist for 1921 is Mr. William M. Burton, to whom the award is made in recognition of his work on the distillation of petroleum under pressure, resulting in the production of enormously large supplies of gasoline for fuel in internal combustion engines and of artificial asphalt which is largely used in the place of the natural product.

The medal will be presented at the meeting of the American Section, Society of Chemical Industry, at Rumford Hall, Chemists' Club, New York City, on January 13, 1922.

Standard specifications for the testing and use of permissible explosives for use in mines, Bureau of Mines Schedule 17, are now before the American Engineering Standards Committee for consideration and approval as tentative American standard. These standards are the result of thirteen years' experience by the Bureau of Mines in testing and assisting manufacturers to develop explosives that offer the minimum hazard, when properly used, in gaseous and dusty mines. The final revision of these rules was made and approved as Schedule 17 on April 8, 1921.

---

[1] THIS JOURNAL, **12** (1920), 857.

The Electrical Conductivity of Solutions of Zinc Sulfate in the Presence of Sulfuric Acid[1]

By **Herman V. Tartar** and **Harmon E. Keyes**

CHEMICAL LABORATORY, UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

In the commercial production of metallic zinc by the electrolysis of zinc sulfate solutions, the energy relations of the zinc cell are naturally of importance, but many of the factors involved are not completely understood. The resistance of the electrolyte has an influence on the electrical power consumed and the amount of heat produced which must be dissipated by proper cooling facilities. The resistance varies with the temperature and the concentration of the zinc sulfate and of sulfuric acid. This variation in resistance is generally met with in practice to a very marked extent, since the process deals with an initial neutral solution of zinc sulfate, and sulfuric acid is formed during the electrolysis. Furthermore, the solution may undergo large temperature changes.

The present paper deals with an investigation of the conductivity of zinc sulfate solutions of the type used in certain typical plants, the observation being made over a temperature range of from 20° to 40° C. The object of the work was to determine the effect on conductivity of temperature, and acid and zinc concentration. Because of recent important work[2] on the deposition of zinc from strongly acid solutions (200 to 300 g. of free sulfuric acid per liter) and at high current densities, the work herein reported deals with both the higher and lower acid concentrations which may be used in commercial practice.

The writers believe that the results secured will possibly be of practical use in the zinc industry. There are few available data on this phase of electrolytic zinc. Furthermore, the calculation of the conductivity of such concentrated mixtures is, in the present state of our knowledge of the degree of ionization of the salt and of the acid in the presence of each other, practically impossible if accurate results are desired.

REAGENTS AND APPARATUS

Purified zinc sulfate was used throughout the experiments. It was made by dissolving "Baker's C. P." zinc oxide in pure sulfuric acid and distilled water, precipitating the metals electronegative to zinc with zinc dust and crystallizing out a portion of the zinc sulfate for use, the mother liquor being kept slightly acid to prevent the formation of basic salts. The zinc sulfate crystals were washed, dried by a suction filter, and assayed for zinc by titration with potassium ferrocyanide.

The sulfuric acid was "C. P. analyzed," the analysis showing no impurities to interfere.

The water used in making up the solutions had a specific conductivity 1.1×10^{-6} reciprocal ohms per cc.

The usual Kohlrausch method was followed in making the conductivity measurements. The set-up consisted of the customary Wheatstone bridge arrangement with slidewire of the drum type, standard resistances, a Leeds & Northrup alternating current generator operating at 1000 cycles per second and giving a nearly true sine-wave current, storage cells for furnishing current to the generator, and a suitable telephone receiver. The conductivity cell was of the cylindrical type, designed to conform approximately to the specifications of Washburn[3] for conductivity of the magnitude here involved. The electrodes were well platinized before use.

In making the measurements at 25° the conductivity cell was placed in a thermostat, the temperature of which was kept constant to 0.02°. For other temperatures the cell was placed in a Dewar flask with thermometer accurate to 0.01°, and the reading was taken when the solution had reached the desired temperature.

The specific gravity determinations were made by the pycnometer method and at a temperature of 25° ± 0.02°. The results are referred to water at 4° as unity.

EXPERIMENTAL

The cell constant was determined by measuring the conductivity of a potassium chloride solution containing 7.43 g. of the salt in 1000 g. of solution, taking the specific conductivity of this solution to be 0.01288 reciprocal ohm at 25°. The cell constant was found to be 6.245. Solutions of known conductivity were tried, the results obtained being very close to the accepted values. The writers estimate that the values given for the specific conductivity of the different solutions do not vary from the correct value by more than 0.5 per cent.

When a solution of zinc sulfate is electrolyzed the reaction taking place may be represented as follows:

$$2ZnSO_4 + 2H_2O = 2Zn + 2H_2SO_4 + O_2$$

The amount of sulfuric acid formed is 1.5 times that of the zinc deposited. In carrying out the conductivity measurements the initial measurement was made on a neutral solution of zinc sulfate. This was followed by the determination of the conductivity of a series of synthetic solutions in which the sulfate content (SO_4) was kept constant and the proportions of acid and of zinc sulfate varied so as to represent the composition of the initial solution at different stages if it had been electrolyzed. Two series of solutions were used; in one the starting point was a solution containing 200 g. of zinc (Zn) per liter and the other 100 g. per liter. The composition of each solution may be easily calculated from the formula:

$$\text{Solution} = ZnSO_4 \text{ required} + (\text{water in original solution} - \text{Zn deposited} \times 0.2755) + H_2SO_4 \text{ required}$$

Assays for sulfuric acid were made as final check on the accuracy of the preparation of the solutions. The values given for specific conductivity are expressed in reciprocal ohms (mhos) per cc. and are in each instance the average of four closely agreeing readings. These results may be converted into resistance in ohms per cu. in., which would be more useful in plant work, by simply dividing the factor 0.3937 by the given conductivity. The conductivity was determined at five temperatures, which cover the range met in actual practice. The composition and specific gravity of the solutions, the values for specific conductivity, and the temperature coefficients (which will be discussed later) are given in Table I. The data on composition are given in three ways; the figures for per cent by weight and grams per liter are included because both of these systems are in common use.

The temperature coefficient of conductivity (β) may be used in calculating the conductivity at any temperature from the expression:

$$\lambda_t = \lambda_{20°}\ (1 + \beta(t - 20))$$

where λ_t = conductivity at $t°$
$\lambda_{20°}$ = conductivity at 20°

In order to show more fully the effect of zinc sulfate and sulfuric acid on the conductivity, runs were made with several solutions, in which one of these substances was kept constant and the other varied. Data for specific conductance of

---

[1] Received July 23, 1921.

[2] Tainton and Pring, U. S. Patents 1,059,233; 1,210,017; 1,247,179; "Tainton Process," *Eng. Min. J.*, **3** (1921), 341.

[3] *J. Am. Chem. Soc.*, **38** (1916), 2431.

Table I—Composition, Specific Gravity, Specific Conductivity and Temperature Coefficients of Conductance of Zinc Sulfate-Sulfuric Acid Solutions

Sample No.	Zn Removed	Zn in New Soln.	H_2SO_4 Produced	H_2O G.	Per cent by Wt. Zn	Per cent by Wt. H_2SO_4	Sp. Gr. 25°/4°	G. per Liter Calculated Zn	G. per Liter Calculated H_2SO_4	Assay H_2SO_4	Temp. Coefficient	Specific Conductance 20°	25°	30°	35°	40°
								Series I								
1	0	200	0	953.6	13.78	0	1.448	200.0	0	...	0.0329	0.0412	0.04755	0.0540	0.0611	0.0683
2	50	150	75.0	939.8	10.70	5.4	1.373	147.0	74.2	73.8	0.01815	0.1313	0.1439	0.1560	0.1676	0.1790
3	100	100	150.0	925.8	7.54	11.31	1.303	98.4	147.3	146.8	0.01442	0.2795	0.3013	0.3225	0.342	0.3601
4	120	80	180.0	920.5	6.14	13.82	1.275	78.4	176.3	175.5	0.01438	0.3533	0.3815	0.4067	0.4325	0.455
5	140	60	210.0	915.0	4.70	16.45	1.249	58.7	205.5	205.0	0.01432	0.437	0.472	0.503	0.5357	0.562
6	160	40	240.0	910.4	3.191	19.15	1.223	39.05	234.2	233.8	0.0145	0.527	0.567	0.607	0.644	0.680
7	170	30	255.0	906.8	2.42	20.55	1.211	29.33	249.0	248.5	0.0138	0.577	0.618	0.661	0.700	0.737
8	175	25	262.5	905.4	2.025	21.28	1.205	24.43	256.5	256.0	0.0139	0.598	0.640	0.682	0.726	0.764
9	185	15	277.5	902.7	1.228	22.70	1.1915	14.68	271.5	269.5	0.0140	0.644	0.692	0.737	0.781	0.824
10	190	10	285.0	901.3	0.8235	23.43	1.184	9.75	278.0	277.2	0.0139	0.668	0.722	0.765	0.812	0.854
11	197	3	295.5	899.4	0.249	24.50	1.175	2.928	288.0	286.5	0.0135	0.706	0.758	0.807	0.855	0.897
12	200	0	300.0	898.5	0	24.93	1.171	0	292.0	292.5	0.0134	0.723	0.775	0.825	0.874	0.917
								Series II								
1	0	100	0	984.8	8.11	0	1.232	100.0	0	...	0.0235	0.0500	0.0557	0.0615	0.0675	0.0735
2	20	80	30	979.3	6.635	2.485	1.201	79.6	29.85	...	0.0130	0.1055	0.1127	0.1197	0.1268	0.1329
3	40	60	60	973.8	5.075	5.075	1.172	59.5	59.5	...	0.00973	0.1783	0.1888	0.1980	0.2060	0.2130
4	60	40	90	968.3	3.456	7.775	1.143	39.51	89.0	...	0.00965	0.2712	0.2852	0.300	0.313	0.3235
5	70	30	105	965.5	2.620	9.18	1.129	29.6	103.6	...	0.01018	0.324	0.343	0.359	0.377	0.390
6	80	20	120	962.7	1.768	10.60	1.116	19.70	118.1	...	0.0108	0.381	0.403	0.424	0.445	0.463
7	100	0	150	957.3	0	13.56	1.089	0	147.7	...	0.0120	0.503	0.536	0.567	0.596	0.624

neutral zinc sulfate were secured to afford a basis for comparison. Since magnesium sulfate may be present in considerable quantity in the commercial solutions the effect of this salt on the conductivity of a mixture of sulfuric acid and zinc sulfate was determined.

The composition of the solutions and the specific conductance are given in Tables II, III, IV, and V. The results secured will perhaps be more readily understood from the curves given. The data in Table I are represented in Figs. 1, 2, 3, and 4. The data of Tables II, III, IV, and V are shown in Fig. 5.

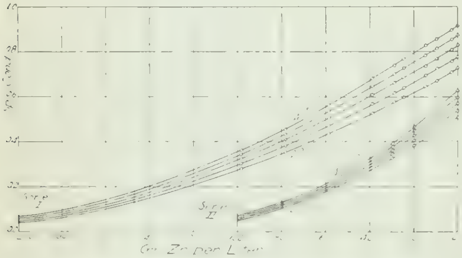


Fig. 1—Change in Specific Conductivity of Zinc Sulfate Solutions (Initial Concentrations 100 and 200 G. per Liter) as Zinc Is Deposited Electrolytically at Different Temperatures. Curves Include Volume Change

In view of the fact that it is common practice to add glue to the electrolyte to obtain better deposits of zinc, the specific conductivity of a sample which contained 230 g. of sulfuric acid and 50 g. of zinc (as zinc sulfate) per liter was determined before and after adding 0.02 and 0.09 g. of gelatin per liter. No change in the conductivity was detected.

Table II—Effect of Zinc Sulfate on Specific Conductivity at 25° of Sulfuric Acid Solution

Sample	Zinc G. per Liter	Specific Conductivity
	H_2SO_4 = 230 g. per liter	
1	0	0.702
2	20	0.627
3	50	0.520
4	80	0.427
5	120	0.322
	H_2SO_4 = 150 g. per liter	
1	0	0.5358
2	60	0.383
3	100	0.301

Table III—Effect of Sulfuric Acid on Specific Conductivity at 25° of Zinc Sulfate Solution (60 g. Zn per liter)

Sample	H_2SO_4 G. per Liter	Specific Conductivity
1	0	0.0446
2	15	0.0784
3	25	0.1025
4	30	0.1145
5	50	0.1643
6	70	0.214
7	75	0.226
8	150	0.383
9	250	0.505

Discussion of Results

In all cases the conductivity of the solutions rapidly increases with the sulfuric acid content. A neutral solution at 200 g. of zinc per liter would have its conductivity increased over fifteen times if the zinc were completely electrolyzed out of solution and an equivalent amount of sulfuric acid were formed. In practice it is not feasible to reduce the zinc content of the electrolyte below 20 g. per liter. When electrolyzed to 20 g. per liter zinc, a neutral solution of zinc sulfate containing 200 g. of zinc (Zn) per liter at 30° C. will have a specific conductivity of 0.71, while a neutral solution of 100 g. per liter of zinc when electrolyzed to the same zinc content will have a specific conductivity of 0.42.

In Fig. 5 is shown the increase in conductivity with acid strength for a solution containing 60 g. zinc per liter. The conductivity increases practically in proportion to the acid strength until about 125 g. per liter of acid is reached, when the rate of increase begins to fall off slightly. However, the highest acid strength shows the greatest conductivity.

Table IV—Specific Conductivity of Neutral Zinc Sulfate Solutions at 25°

Sample	Zn G. per Liter	Specific Conductivity
1	10.0	0.01258
2	30.0	0.02865
3	60.0	0.0446
4	80.0	0.05115
5	100.0	0.0557
6	120.0	0.05685
7	150.0	0.0560
8	180.0	0.0515
9	200.0	0.04755

Table V—Effect of Magnesium Sulfate on Specific Conductivity at 25° of Mixture of Zinc Sulfate and Sulfuric Acid (Zn = 55 g., and H_2SO_4 = 230 g. per liter)

Sample	Mg. G. per Liter	Specific Conductivity
1	0	0.508
2	5	0.461
3	10	0.419
4	15	0.379

A solution carrying 117 g. per liter H_2SO_4 and 20 g. of zinc has a specific conductivity of 0.46 at 40° C., which would be a high temperature for regular operating work with the degree of electrolyte purification possible at the present time. However, a solution containing 263 g. H_2SO_4 per liter and 20 g. Zn has a specific conductivity of 0.615 at 20°, a temperature lower than that generally employed. This shows that strong acid electrolytes, at a moderately low temperature, have a much higher conductivity than weak acid solutions even when raised to a temperature higher than is generally considered permissible. The curves in Fig. 5 show that with the neutral solution the point of maximum conductivity

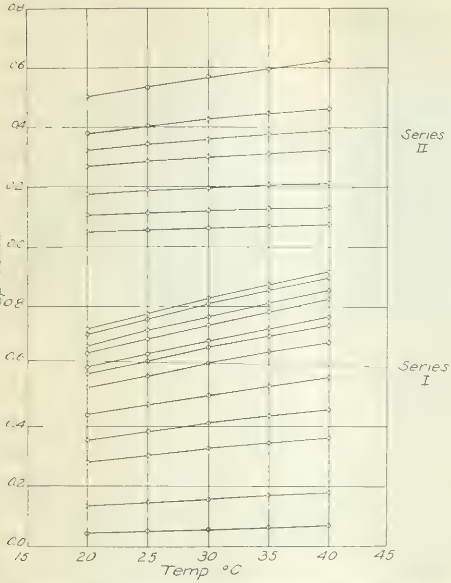
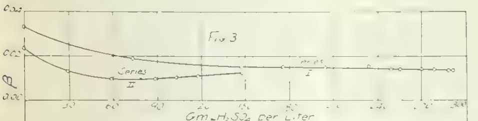


Fig. 2—Effect of Temperature on the Specific Conductivity of Solutions of Series I and II

is reached at 120 g. zinc per liter, and that the conductivity of strong sulfuric acid solutions is diminished by zinc sulfate. This increase in resistance, due to the addition of zinc, is more marked the stronger the acid and is probably caused by the increased sulfate (SO_4), which may lower the concentration of the hydrogen ion by repressing the ionization or by forming complex compounds with the acid. If this be true, the presence of other metallic sulfates should produce a similar effect. The data in Table V, which are shown graphically in Fig. 5, substantiate this statement and show that the resistance of the given solution is increased 25 per cent by adding 15 g. of magnesium per liter in the form of sulfate.



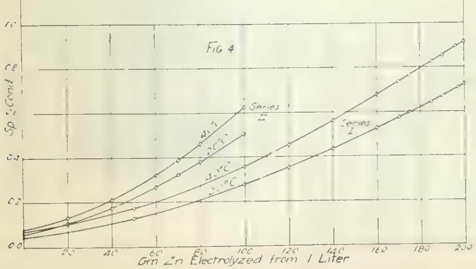


Fig. 3—Variation of Temperature Coefficients of Specific Conductivity of Solutions of Series I and II

Fig. 4—Change in Specific Conductivity of Zinc Sulfate Solutions of Series I and II at 20° and 40° with Increase of Zinc Deposited (the Acid Strengths Coincide). Curves Independent of Volume Change

The two series in Table I are plotted in Fig. 4, with the acid strength coinciding. The solutions with lower zinc concentrations have higher conductivity than those of the same acid strength and higher zinc content. However, as shown in Fig. 1, when the same data are plotted with the zinc concentrations coinciding, the higher acid strengths give the greater conductivity, and therefore the highest conductivity is ultimately reached with the solutions which originally contained the greatest concentration of zinc.

From the results in Table I it is evident that a volume change accompanies the electrolysis, there being an actual *increase* in volume notwithstanding a loss of zinc and oxygen. Theoretically, when 200 g. of zinc have been deposited from a liter the resulting solution assays only 292 g. per liter of H_2SO_4 instead of 300. When 100 g. of zinc are electrolyzed out of solution the gain in volume is about 1.5 per cent. This is a fact not generally considered in plant control.

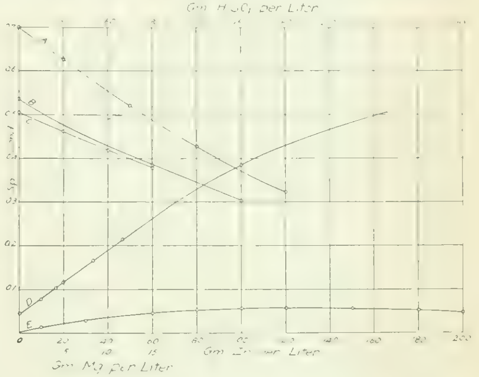


Fig. 5—Influence on Specific Conductivity of Variations of Sulfuric Acid or Metal Sulfate Content

A—H_2SO_4, 230 g. per liter, varying $ZnSO_4$
B—H_2SO_4, 150 g. per liter, varying $ZnSO_4$
C—$ZnSO_4$ and H_2SO_4, 55 g. Zn and 230 g. H_2SO_4 per liter, varying $MgSO_4$
D—$ZnSO_4$, 60 g. Zn per liter, varying H_2SO_4
E—Neutral $ZnSO_4$

The increase of conductivity with temperature which is given in Fig. 2 is a nearly linear function. The temperature coefficients vary with the strength of the original neutral solution and the extent of electrolysis (Fig. 3).

SUMMARY

1—The conductivity of zinc sulfate electrolyte greatly increases with sulfuric acid concentration.

2—The conductivity of sulfuric acid is diminished by the addition of zinc sulfate. Adding magnesium sulfate to a strongly acid zinc sulfate solution causes an additional decrease in conductivity.

3—The temperature coefficients of conductivity vary and are a function of the acid and zinc concentration.

4—The addition of 0.02 to 0.1 g. of gelatin per liter has no influence on the conductivity.

5—The conductivity of an acid zinc sulfate solution appears to be due largely to hydrogen ion, and lowering of the hydrogen-ion concentration by the addition of metal sulfates decreases the conductivity.

6—The deposition of zinc is accompanied by an increase in volume, amounting to 1.5 per cent for each 100 g. of zinc deposited.

Recent Development in the Art of Rubber Microsectioning[1]

By Henry Green

New Jersey Zinc Co., Palmerton, Pa.

There has lately appeared an article[2] by Messrs. Depew and Ruby in which the authors point out the desirability of studying the nature and dispersion of compounded pigments in rubber microsections.

Their method of preparing the sample for sectioning, by freezing with carbon dioxide and liquid air, entails certain disadvantages which are difficult or quite impossible to overcome. Chief among these are the annoyances encountered in obtaining, transporting, and keeping liquid air. In addition, the method usually necessitates the use of large amounts of carbon dioxide, before a satisfactory section can be secured. The main drawback is met in the comparatively high temperature of the knife. As the blade passes over the specimen, the heat it (the blade) contains is partly transferred to the frozen rubber causing it to thaw, with a consequent change in volume, thus making it impossible to regulate the thickness of section. This fact is particularly objectionable when it is desired to obtain the thin sections required for the examination of rubber containing high percentages of gas black. Briefly, the method fails economically, both in respect to expense and time.

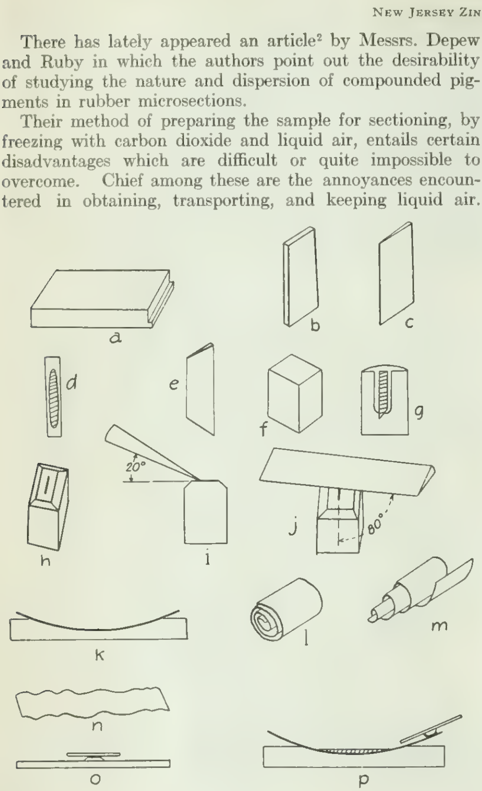


Fig. 1

After stating the objections to the freezing method it would hardly be fair to omit emphasizing its chief virtue, *i. e.*, the fact that the specimen is not chemically prepared, and therefore a possibility of destroying the rubber structure or influencing the dispersion of the pigment is eliminated. For this reason, alone, it is not desirable to abandon entirely the idea of employing the freezing method at times.

The New Method

This method is purely a chemical one. The elasticity of the rubber is destroyed and a proper rigidity acquired by revulcanization with a very dilute carbon tetrachloride solution of sulfur chloride.

It is essential that the specimen be of proper size and shape for sectioning. From a block of the rubber to be examined, (*a*, Fig. 1) either a rectangular or wedge-shaped corner is cut (*b* and *c*), approximately 0.5 × 4 × 20 mm. in size. This piece is placed in the vulcanizing solution (the strength of which is discussed below) and treated for a length of time that will vary according to the nature of the rubber, thickness of the section, and, of course, the concentration of the solution. At stated intervals, the specimen is removed and examined by slicing off a small portion of the end and testing the hardness with a needle point.

The ability to recognize the proper degree of hardness is easily acquired with practice; to attempt to describe it is difficult. As a rule there should be no indication of elastic recovery where the rubber has been scratched or depressed. Above all there should be no soft unvulcanized core, as shown at *d*. On the other hand, the specimen must not be so hard that it cracks and crumbles upon cutting, but rather it should slice as easily as a piece of soft wood in the direction of grain.

Assuming that the specimen is correctly vulcanized, the next step is to allow it to become thoroughly dry (preferably by vacuum treatment) and then to sharpen it at one end, as at *e*, simply for convenience in inserting it in the paraffin mounting block. This block, *f*, is rectangular in shape and roughly 15 × 15 × 30 mm. It is clamped in a vise and a hot nail or other convenient instrument pushed into its upper end to a depth of about 18 mm., to produce a cavity in which the specimen is placed. The pointed end *e* must be pressed firmly into the paraffin and the face of the block covered with a few drops of melted paraffin (Fig. 1, *g*). After cooling, the block is trimmed as shown at *h*. It is then ready to be sectioned.

The knife must be of the flat-faced type and make a vertical angle with the specimen of about 20° and a horizontal angle of approximately 80° (Fig. 1, *i* and *j*). Not less than ten sections should be cut at a time. They will adhere to form a ribbon which is easily removed to a watch glass, *k*. A small hand glass is employed to count the number of sections imbedded in the ribbon in order to note whether the microtome has "skipped" or not. In case it has, it is then impossible to ascertain the thickness of the section from the microtome setting.

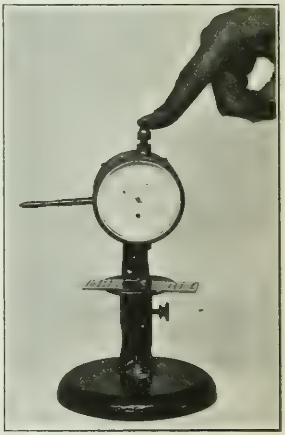


Fig. 2

The paraffin adhering to the microsection is now removed with a few cc. of toluene. The specimens, upon examination,

---

[1] Presented before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] "Some Microsections Cut from Vulcanized Rubber Articles," This Journal, 12 (1920), 1156.

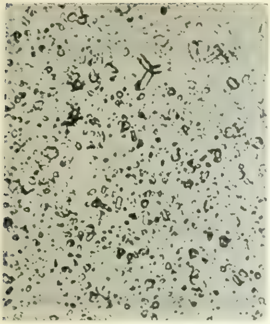


FIG. 3

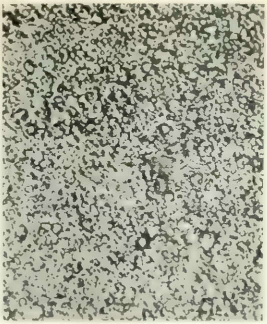


FIG 4

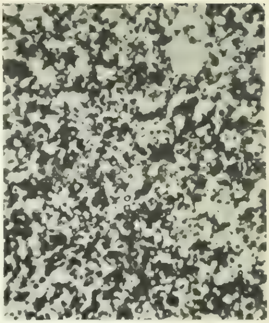


FIG 5

will be found to be curled either in the manner shown at *l* or at *m*. If the former is the case, they will be difficult to uncurl and the horizontal angle of the knife must be made more acute so as to prevent this form of curling. Next the sections are removed from the toluene by sliding them up to the edge of the glass with the aid of the needle.

If the sections are thick (3–5μ) they will probably become detached from the glass upon drying and are easily transferred to the microscope slide. The mounting medium is piperine (never Canada balsam).[1] A few small crystal fragments of this material are placed on the slide and warmed till melted. Upon cooling, piperine will remain plastic and sticky for some time. While in this condition, the section is placed on its surface and covered with a glass (Fig. 1, *n*). Upon alternately warming and pressing on the cover glass the excess of piperine is gradually squeezed out.

The specimen is next examined with a low power microscope. If it is found to be badly wrinkled, as shown at *o*, or to contain objectionable air bubbles, the slide is transferred to a hot plate and heated for a minute or so till the piperine is quite fluid. While in this state it is necessary to apply a comparatively high pressure in order to remove the air bubbles and at the same time to flatten the section as much as possible. The author has found a thickness gage convenient for this purpose. The slide is placed on the stage and pressure applied with the finger on the upper end of the plunger (Fig. 2). After cooling, the mount is ready to be labeled and examined.

If the section is quite thin (0.5–1.5μ) it will not become detached from the watch glass upon drying. In such a case it is sometimes possible to detach it with the needle point. If this fails it is necessary to resort to the following method: First melt the piperine on the microscope cover glass, instead of the slide. Invert it so that the drop will hang downward. Upon solidification press the drop against the section, as shown at *p*, Fig. 1. The specimen may become slightly damaged by this process but it will adhere to the piperine and can now be mounted by the method previously described.

Reference has been made to the strength of the vulcanizing solution. This will vary with the kind of rubber to be treated. A zinc oxide tread, for instance, can be sufficiently prepared in 5 to 10 min. in a carbon bisulfide (N. B., not carbon tetrachloride) solution which contains just enough SCl to impart to it an easily discernible yellow tint, perhaps several drops in 50 cc. of solution. If this is found to be too weak the strength may be increased or the specimen sliced thinner. The best concentration is in all cases quickly and easily found by trial.

In preparing rubber which is compounded with gas black, the solution should be made with CCl_4, as otherwise brittleness is liable to ensue. Carbon tetrachloride solution acts much more slowly and consequently should be made stronger —15 drops to 50 cc. In some cases it is necessary to allow treatment to continue from 1 to 3 hrs. before the specimen is hardened completely. Any number of samples, however, can be prepared together so that the time lost is not a serious factor.

SOME RESULTS OBTAINED WITH THE SCl METHOD

A rubber microsection made as described will be approximately 0.5 × 4.0 mm. in area. On account of the minute size of the compounded pigment particles it has been found most convenient to employ for examination a magnification of at least 1500 diameters.

While a microsection of this size may seem rather small to show all the characteristics that a particular rubber sample possesses, in reality it will be found amply large enough. If the field of the microscope were so extended that it could give a single view of the entire section it would appear (at 1500 diam.) to be a strip, in round numbers, 3 ft. by 20 ft. in area.

Sections prepared by the sulfur chloride method possess beautiful transparency and uniformity in thickness. They are practically ideal for visual examination where it is always possible, by varying the fine adjustment, to bring any part of the mount (and at any depth) into focus, hence the slight lack of flatness, which these sections often have, is not objectionable.

A section which is not perfectly flat is a difficult one to handle from a photomicrographic viewpoint; however, most specimens contain areas that are sufficiently free from this defect so as to enable one to obtain fairly satisfactory photomicrographs.

Fig. 3 is a zinc oxide tread. No difficulty is experienced in obtaining good sections of rubber compounded with normal amounts of this material. On account of its transparency these sections may be cut quite thick (3–5μ).

Fig. 4 is a specially prepared sample containing 100 volumes of rubber to 100 volumes of zinc oxide. Even with this high percentage of oxide the pigment particles are uniformly distributed, showing absence of aggregation. The section was not difficult to make.

No photomicrograph can do justice to the sections presented in Figs. 5 and 6. The former shows lampblack, always existing in rubber flocculated into small groups with clear water-white spaces between. The individual particles are not discernible as they are never found dispersed. A great deal of the detail in this section cannot be seen in the

---

[1] In a rubber section mounted in balsam, zinc oxide becomes quite invisible, excepting the largest particles, which are always readily seen.

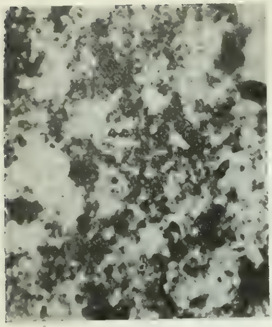


Fig. 6

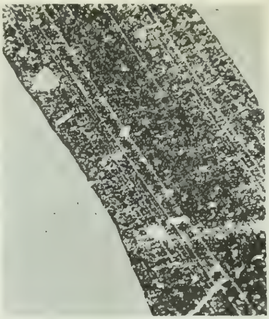


Fig. 7

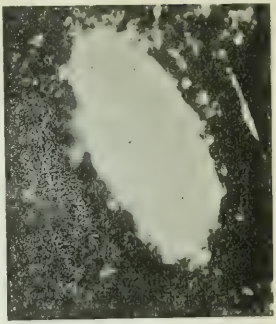


Fig. 8

photomicrograph. Fig. 6 is rubber compounded with gas black. This black is found much better distributed than the former, though one inexperienced in work of this nature might easily infer otherwise from a comparison of the photomicrographs. Here again (in Fig. 6) much of the detail observable with visual examination is lost in the attempt to reproduce it photomicrographically. As a matter of fact, a more difficult subject than rubber containing normal amounts of gas black cannot be found in the entire field of photomicroscopy. There is no difficulty whatever in readily distinguishing between a rubber compounded with lampblack and another containing gas black, upon microscopic examination.

Fig. 7 shows a tread containing gas black and clay. The magnification is but 67.5 diameters. The clay is best examined between crossed nicols where it shows extinction and interference colors. Fig. 8 is the same sample magnified 1500 diameters in order to observe the gas black, individual particles of which can be seen along the edge of the clay particle.

Frequently, rubber compounded with gas black will be found to contain innumerable pocket-like spaces absolutely devoid of pigment particles. Fig. 9 shows a section of this kind. So far it has been impossible to determine whether these spaces are empty or contain a substance which the gas black particles are unable to penetrate. Fig. 10 is a rough torn edge of a similar section showing a sponge-like structure, due to these pockets.

Growth of crystalline substance in rubber is an interesting procedure to study. Fig. 11 is a section containing crystallized para toner. This substance is first dissolved in melted paraffin in which the rubber is soaked before sectioning. The sample was not treated with sulfur dioxide, no pigment being present to interfere with the transparency, hence a thick section (100–200μ) could be used. The paraffin itself will produce sufficient rigidity to make possible the cutting of these abnormally thick sections.

The microsection was next washed with toluene to remove the paraffin and then dried and mounted in glycerol. If such a mount is examined immediately it will be found that the para toner has crystallized and if the process of crystallization is to be studied, solution must first be obtained by warming the slide. The rubber will act as a liquid solvent and cause complete solution of the toner. When recrystallization commences it can be studied microscopically, using a low power objective. The material sends out branches apparently with perfect freedom just as though it were suspended in a liquid medium instead of a solid one.

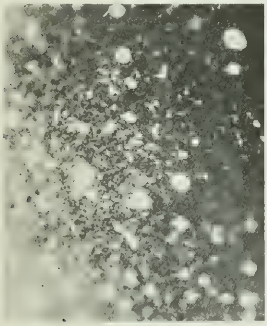


Fig. 9

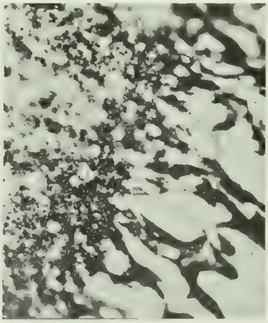


Fig. 10

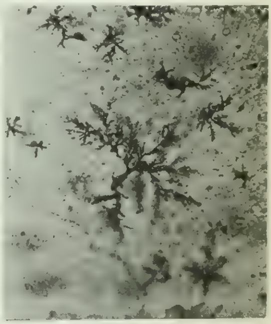


Fig. 11

In conclusion the author wishes to state that he has constantly borne in mind, while preparing rubber microsections by the sulfur chloride method, that the rubber is given a chemical treatment that might possibly produce effects not present in the untreated original specimen. In order to ascertain if undesirable alterations had appeared it was necessary to make comparisons with specimens prepared by the freezing method. Wherever it was possible to do this the results given by the two methods were found to be identical.

Acknowledgment

The author wishes to acknowledge his indebtedness to Mr. Howard M. Cyr for valuable aid received from him during the preparation of this paper.

The Relation between Coefficient of Vulcanization and Mechanical Properties of Vulcanized Rubber[1]

By **O. de Vries**

CENTRAL RUBBER STATION, BUITENZORG, JAVA

Our scientific knowledge of rubber and its vulcanization is still so deficient that even a number of the most fundamental points on which rubber testing should be based are insufficiently cleared up. For instance, it still forms a point of discussion whether the mechanical properties or the coefficient of vulcanization are the most important in judging the state of cure of vulcanized rubber. Some argue that the mechanical properties of the vulcanized article are the only ones that interest the buyer, while he is indifferent as to how much sulfur has combined with the rubber to reach the degree of elasticity and strength that suits his purpose. Others point out that the mechanical properties are not constant in a colloid like rubber, while the coefficient of vulcanization is not changed by mechanical treatment and is also independent of aging—or at least nearly so at ordinary temperatures—so that in general the coefficient is a better indication of the state of cure to which the rubber was originally brought.

Discussion on this point may well rest till sufficient experimental material has been gathered to clear it up definitely; elsewhere[2] we have summarized the present situation as follows: "As the determination of the coefficient of vulcanization means a considerable amount of additional work, and gives no actual gain in the routine of our testing of estate samples, we have not included it in our regular tests," and further, "When one wants to gain as complete an insight as possible into the properties of so complicated a substance as vulcanized rubber, both coefficient of vulcanization and mechanical properties have to be taken into consideration."

EFFECT OF ADDED ACCELERATORS ON COEFFICIENT OF VULCANIZATION

From the latter standpoint, one of the first subjects for further research is the difference in coefficient of vulcanization for different types of rubber, cured to the same mechanical properties (position of the stress-strain curve). It has been remarked by many investigators that, when curing to a fixed cure as judged by the stress-strain curve, the coefficient of vulcanization may vary over a rather wide range. An especially striking example has been recently published by D. F. Cranor,[3] who found that the coefficient for a given curve was influenced largely by the addition of accelerators. For instance, when cured to a certain curve, mixtures with and without an accelerator gave the following coefficients:

SAMPLE	Time of Cure Minutes	Coefficient of Vulcanization Per cent
Original smoked sheet.....	198	4.9
Same, with 0.5 per cent hexamethylenetetramine.	35	1.8
Same, with 0.5 per cent dimethylamine derivative..................	2.4	0.9

EFFECT OF NATURAL ACCELERATORS

The accelerators increase the rate of cure enormously, and at the same time the coefficient for given mechanical properties decreases markedly. This may be explained in several ways. The organic accelerators may have a stronger accelerating effect on the processes that alter the mechanical properties than on the combining of the rubber with sulfur. Or, the very short time during which the rubber is exposed to the high temperature of vulcanization may avoid the disintegrating effect of heat (which is opposite to the stiffening effect of vulcanization). Be this as it may, if powerful organic accelerators give such a marked difference in the coefficient of vulcanization for a fixed curve that the question arises, what may be the effect of the so-called natural accelerators in plantation rubber? These accelerators are either constituents of the latex as it comes from the tree, or decomposition products formed from the non-rubber constituents during preparation. They are supposed to be amines or amino acids, and are undoubtedly very powerful accelerators, since they give a marked increase in rate of cure although present in the rubber in only very small quantities.

Ordinary plantation rubber, tested in pure rubber-sulfur mixtures, indeed shows the phenomenon of differences in coefficient of vulcanization for fixed mechanical properties, but the variation is by no means as large as in the above example.

A. van Rossem[1] studied this variation for a large amount of statistical material. For our purpose his results may be summarized as follows: Taking as the basis of comparison a stress-strain curve for which the average coefficient of vulcanization is 3.0, out of a number of samples of ordinary first quality crepe or smoked sheet, 50 per cent will not show a larger variation in coefficient of vulcanization than 0.25. For the bulk of plantation rubber, therefore, the relation between stress-strain curve and coefficient is rather close.

EFFECT OF TIME OF CURE ON COEFFICIENT OF VULCANIZATION

The question further arises, which types of plantation rubber show a coefficient higher than the normal, and which show a lower one?

B. J. Eaton and F. W. F. Day[2] found the coefficient of vulcanization for standard mechanical properties (their optimum curve) to be:

	Standard Time of Cure Hours	Coefficient of Vulcanization Per cent
Ordinary crepe............	3.25	4.1 –4.5
Crepe from matured rubber	1.25	4.65–5.1

Matured rubber is prepared by keeping the coagulum in the wet state for some time. A decomposition then sets in, and the protein decomposition products cause an increased rate of cure. Eaton and Day therefore find an increase in coefficient, the more natural accelerator the rubber contains. H. P. Stevens[3] for three samples of rubber finds the following figures for the coefficient of vulcanization at fixed positions of the curve.

SAMPLE	POSITION OF CURVE Load in Kg./Sq. Mm. at 1000 Per cent Length 700	900	1100	1300
	COEFFICIENT OF VULCANIZATION			
Smoked sheet.................	1.8	2.1	2.4	2.7
Crepe.........................	2.3	2.65	2.95	3.25
Crepe from matured rubber....	2.4	2.85	3.1	3.2
	TIME OF CURE (Min.)			
Smoked sheet.................	77	90	103	116
Crepe.........................	113	132	150	168
Crepe from matured rubber....	57	70	77	81

Up to a coefficient of 3.1 the rapid-curing matured rubber shows higher figures than the ordinary crepe, as in Eaton and Day's experiments. The sample of smoked sheet, though curing more quickly than the crepe, shows throughout a much lower coefficient for the same curves.

---

[1] Received May 2, 1921.

[2] O de Vries, "Estate Rubber, Its Preparation, Properties and Testing," **1920**, 489, 531.

[3] *India Rubber World*, **61**, 137; *India Rubber J.*, **58**, 1199. For further examples see A. van Rossem (*Comm. Gov. Inst. Delft*, **1917**, 213; D. F. Twiss and S. A. Brazier, *J. Soc. Chem. Ind.*, **39** (1920), 125; H. P. Herens, *India Rubber World*, **62**, 720.

[1] Comm. Gov. Inst. for Advising the Rubber Trade (Delft), V, 164.

[2] *J. Soc. Chem. Ind.*, **36** (1917), 1116.

[3] *Ibid.*, **37** (1918), 280*t*.

The author gathered some material to make a further study of this point. In the first place, we may mention some samples of ordinary crepe of different rate of cure. These gave:

SAMPLE	Standard Time of Cure Minutes	Coefficient of Vulcanization
660	85	5.1
602	90	5.0
1897	94	5.0
1667	115	4.4
1204	120	4.75
1602	122.5	4.4

The coefficient of vulcanization is determined for our standard state of cure,[1] for which the length at a load of 1.30 kg. per sq. mm. is 990 per cent. The more quickly curing crepes, which contain more of the natural accelerators, show a higher coefficient of vulcanization in accordance with the results of Eaton and Day and of Stevens.

Some specially prepared samples of abnormal composition gave the following figures:

NO.	SAMPLE	DESCRIPTION	Standard Time of Cure Minutes	Coefficient of Vulcanization
1	2467	Matured rubber	30	4.9
2	1883	Latex evaporated to dryness	65	5.1
3	2459 W	Ball smoked after Brazilian method	70	5.25
4	2365 DW	Ball smoked after Brazilian method	70	5.1
5	2365 BW	Ball smoked after Brazilian method	80	5.15
6	2494 A	First clot in partial coagulation	85	5.3
7	2494 B	Rest after partial coagulation	115	.4.35
8	2494 C	Ordinary coagulation	115	4.65

The first sample is matured rubber (slab rubber) and may be classed among those with the greatest rate of cure as yet known. Like all matured rubber it contains natural accelerators formed by decomposition of proteins, but less non-rubber constituents than ordinary crepe, as part of the serum substances has been decomposed and escaped in gaseous form (loss in weight about 1.5 per cent). The coefficient of vulcanization is higher than normal.

The second sample is also quick curing; it contains all the latex constituents, being prepared by rapid evaporation of latex by hot air (Kerbosch process);[2] no maturation or decomposition of serum substances has taken place. The coefficient of vulcanization is higher than normal, as in the foregoing case.

Samples 3 to 5 have been prepared after the Brazilian method (smoked balls), Sample 3 by a native smallholder and Samples 4 and 5 as part of the output of a large European estate. The samples were 0.5 to 1 yr. old when tested, and showed the ordinary rather rapid rate of cure of balls of that age.[3] Smoked balls retain somewhat more serum substances than ordinary crepe and smoked sheet, but they contain by no means all latex constituents, as a large amount of serum drips out during and after preparation. Maturation takes place slowly in the balls, bringing the time of cure from 100 to 50 min. in the course of 2 yrs.[4] The coefficient of vulcanization for this type is higher than the average and nearly the same as in former cases.

Sample 6 is prepared from the first clot obtained in partial coagulation. Such rubber contains more by-substances than ordinary crepe; it cures more quickly (though no maturation has taken place). The properties of Samples 6 to 8 were:[5]

No.	Moisture	Ash	Aqueous Extract	Acetone Extract	Viscosity	Tensile Strength	Slope
6	1.40	0.35	0.51	4.2	35	1.40	33
7	0.64	0.17	0.13	2.7	23	1.39	36
8	0.93	0.28	0.11	3.2	30	1.46	36

In this case also the coefficient of vulcanization is higher than normal for the more quickly curing sample.

Though these four types of quick-curing rubber are prepared in totally different manners, and show large differences in composition (both in amount of serum substances and in accelerator formed by maturation), the excess in coefficient of vulcanization is nearly the same in all cases.

Plantation rubber therefore seems to show a higher coefficient of vulcanization than normal when it is quick curing, independent of whether the quicker cure is caused by unchanged latex constituents or by decomposition products formed by maturation. The few exceptions to this rule deserve further study.

In future investigations of this kind it will be interesting to push the analysis further by determining not only the total combined sulfur in the ordinary way, but by differentiating between the sulfur bound by the rubber and by the nonrubber constituents as proposed by W. J. Kelly.[1] Perhaps a difference as between Samples 7 and 8 might be cleared up in this way.

SUMMARY

The natural accelerator or accelerators in rubber cause an increase in coefficient of vulcanization for fixed mechanical properties, which amounts to about 0.5 for all types of quick-curing rubber, independent of their composition. The natural accelerators therefore act in exactly the opposite way to the artificial accelerators about which data are now available.

The effect of the natural accelerators on the coefficient for a fixed curve seems to be much less pronounced than in the case of those artificial accelerators.

Organization of the Natural Resources Production Department of the Chamber of Commerce of the United States is just being perfected. The department is preparing a very active program in an effort to render constructive service to the raw material industries, supplementary to the work of the various trade associations. It is believed that great assistance can be rendered to the industries and to the public by conducting a campaign of education intended to enlighten the public on the vital problems of natural resource activities. The following advisory committee has been appointed: C. S. Keith, Central Coal & Coke Co., Kansas City, chairman; J. H. Ross, Exchange Supply Co., Winter Haven, Fla.; J. E. Spurr, *Engineering and Mining Journal*, New York City; Christy Payne, Peoples & Hope Natural Gas Cos., New York; E. T. Meredith, former Secretary of Agriculture, Des Moines, Iowa; Sidney J. Jennings, United States Smelting, Mining & Refining Co., Boston, Mass.; R. V. Norris, mining engineer, Wilkes-Barre, Pa.; Van H. Manning, American Petroleum Institute, New York; and William H. Davis, Mid-Continent Oil & Gas Association, Bartlesville, Okla.

Canadian pulp and paper exports for September reached a value of $9,457,027, a decline of $7,033,665 as compared with September 1920 and an increase of $51,635 over August 1921. Exports of newsprint for the month amounted to 1,224,136 cwt., compared with 1,212,225 in September 1920. Countries of destination were:

	Paper	Pulp
United Kingdom	$ 116,591	$1,221,245
United States	5,249,548	2,175,937
Other countries	408,468	285,328

Comparative figures for the first six months of the fiscal year show:

	Paper	Pulp	Total
1921	$33,379,508	$15,804,159	$49,183,667
1920	43,025,764	44,217,712	87,243,476
1919	27,119,246	16,626,726	43,745,972

Pulpwood exported to the United States for the first six months of the year were as follows:

1919	515,444 cords	$5,089,693
1920	653,856	7,803,332
1921	421,388	5,546,785

---

[1] See "Estate Rubber, Its Preparation, Properties and Testing," 463, 542.

[2] "Estate Rubber," p. 436.

[3] *Ibid.*, pp. 422–431.

[4] *Ibid.*, pp. 422-431

[5] Compare *Arch. Rubbercultuur*, **1** (1917), 185; *J. Soc. Chem. Ind.*, **38** (1919), 92; *India Rubber J.*, **57** (1919), 1164; "Estate Rubber," p. 389.

[1] THIS JOURNAL, **12** (1920), 875.

The Properties and Action of Enzymes in Relation to Leather Manufacture[1]

By **Joseph Turney Wood**

TURNEY BROTHERS, LTD., NOTTINGHAM, ENGLAND

THE SOAKING PROCESS

Enzymes occur in and influence almost all the operations of tanning from the moment that the skin is flayed until it is dried out in the form of leather. The fresh skin contains a number of enzymes about which very little is known and other enzymes are soon formed by bacteria. We shall not consider these in any detail, as we may assume that the raw skin has been properly preserved after flaying and before coming into the hands of the tanner, but in the soaking process we meet with enzymes secreted by a variety of species of bacteria. Most of these bacteria liquefy gelatin by means of the proteolytic enzymes which they secrete, and consequently they attack the skin. So far as the writer knows, the bacteria of the soaks have not been specially studied except by Andreasch,[2] who isolated a number of species of bacteria from the soaks. He identified the following:

B. fluorescens liquefaciens (Flügge)
B. megaterium (de Bary)
B. subtilis
B. mesentericus vulgatus
B. mesentericus fuscus
B. mycoides (Flugge)
B. liquidus (Frankland)
B. gasoformans (Eisenberg)
White bacillus (Maschek)
Proteus vulgaris
Proteus mirabilis
B. butyricus (Hueppe)
White streptococcus (Maschek)
Worm shaped streptococcus (Maschek)
Gray coccus (Maschek)

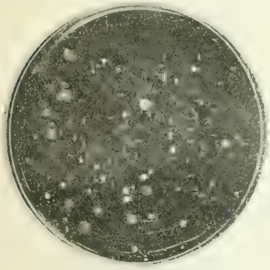


FIG. 1—TYPICAL PLATE CULTURE ON GELATIN OF SOAK USED FOR SOFTENING DRY SHEEP SKINS

All these may be classed as putrefactive organisms, and they secrete a variety of enzymes, some of which act energetically on the hide substance. Fig. 1 shows a typical plate culture on gelatin of a soak used for softening dry sheep skin, in which no chemicals have been used. The development of the colonies had to be stopped by the application of formalin vapor before many of the species had time to develop; otherwise the whole plate would have been liquefied. In view of the fact that the enzymes in the soaks are nearly all derived from bacteria, it is evident that the soaking should be carried out under antiseptic conditions as far as possible.

Rideal and Orchard[3] examined the action of *B. fluorescens liquefaciens* on gelatin to which was added 10 per cent of Pasteur's solution to serve as nutrient medium. The gelatin was completely liquefied in 3.5 days. It was shown that the liquefaction of gelatin was due to an enzyme, or enzymes, secreted by the bacteria. The liquefied gelatin was alkaline and had a slight putrefactive odor, but contained no hydrogen sulfide. A notable feature was the small amount of ammonia and volatile bases produced; only 0.2 g. of ammonia per 100 cc. were produced even after 16 days' incubation. The liquefaction of gelatin by pancreatic trypsin takes place with much greater rapidity; 0.2 mg. of the enzyme preparation will liquefy 5 cc. of 4 per cent gelatin in 30 min. at 39°.

THE LIME LIQUORS

In a lime liquor through which skins have passed, there are enzymes present. The writer is inclined to believe that some of these are from the skin itself, at least when fresh market skins are worked, as, for example, the tissue enzymes, but nothing definite is known of these. Bacteria, however, develop in the limes. *B. prodigiosus* and *Micrococcus flavus liquefaciens*, both of which are known to produce proteolytic enzymes, have been identified. These enzymes decompose the dissolved skin substance into gelatones (gelatin-peptones) and eventually into amino acids, caproic acid, and ammonia. It is very probable that the enzymes in the limes act in the same way as the enzymes in the sweating process of unhairing, but in the limes the process stops short of putrefaction, whereas in the sweating stove it may go on until the skin is run on the grain.

THE BATING PROCESS

The investigation of the action of the bates or puers has proved of great interest and has resulted in the use of scientific methods depending on the use of commercial enzymes in leather manufacture. The object of bating or puering is to render the skins, and the resulting leather, soft and supple. Skins which have undergone the liming process must be thoroughly freed from lime before going into the tan liquors, and for light and soft leather they must be reduced or "brought down" so that the elasticity or resilience of the skin fibers is got rid of, and the skin when tanned can be stretched without springing back. In the case of the old manure bates for light leathers, this is done by passing the skin through a bate or puer composed of an infusion of dogs' dung in water at a temperature of 35° to 40° until the desired result is obtained. This condition is known to the workman by the feel of the skin. The process has been in use from the very earliest times, but until comparatively recently no explanation of the action of the dung bates was satisfactory.

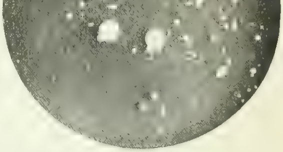


FIG. 2 TYPICAL PLATE CULTURE ON GELATIN OF PURE LIQUOR

Thirty years ago, when the author commenced the investigation of the action of the dung bate in the manufacture of light leathers, he came to the conclusion that a great part of the bating effect was due to the action of proteolytic enzymes on the skin in conjunction with ammonium salts present in the bate. The latter not only combined with the lime remaining in the skin, but also acted as activators for the enzymes. Numerous experiments were made on skins both in the presence of growing bacteria and of the products of the bacteria, precipitated by alcohol, and it was found that when suitable ammonium salts were present the bating action in both cases was similar.

There is little doubt that every variety of enzyme, hydrolyzing, oxidizing, ammoniacal, etc., is produced by bacteria. The production of enzymes by bacteria was observed by Wortmann in 1882, and Fermi and others have investigated the enzymes of the bacteria which liquefy gelatin. Since the bacteria in the bate produced these enzymes, the first idea was to use them in practice in a scientific way. In conjunction with Prof. H. Becker, we manufactured a bacterial bate "Erodin," which the writer believes was the first attempt to apply the use of pure cultures of bacteria in the leather industry. The bacterium used was a variety of *B. coli* isolated from dog dung. Harden[1] has shown that this bacterium produces at least three enzymes.

---

[1] Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] *Gerber*, **1895-6**.

[3] *Analyst*, October **1897**.

An investigation of the enzymes contained in dog dung showed that five different enzymes were present:[2]

1—A peptic enzyme resembling stomach pepsin.
2—A tryptic enzyme, or enzymes, resembling pancreatic trypsin.
3—A rennin (coagulating enzyme)
4—An amylolytic enzyme.
5—A lipase.

In view of the fact that the bate solution is alkaline, it seemed pretty certain that trypsin must be the principal enzyme acting, and it is this enzyme which has been applied practically in the manufacture of artificial bates.

It must be clearly understood that, although the enzymes and ammonium compounds are the chief bodies acting on the skin in the dung bate, they are not the only bodies taking part in the process. As the writer has shown, there are many other bodies in the dung which act in a way at present not understood. Among these the fats, soaps, and phosphates are, in his opinion, important. Among other enzymes present in the dung, the lipases have a considerable effect in emulsifying and hydrolyzing the fats.

Skins which have been overlimed are bated more effectively in a dung bate than in an artificial, enzyme bate, and this must be due to some constituents in the dung bate which are absent from the enzyme bate. It has further been shown that excessive liming so alters the chemical constitution of the hyaline membrane as to render it capable of being attacked by trypsin.

Rosenthal[3] states that elastin is digested in the bating process; and more recently Seymour-Jones has been able to show that the elastin is contained principally in the grain layer.

Elastin is the characteristic constituent of the elastin fibers which remain after treating the skin with boiling water, caustic alkali, dilute hydrochloric acid, alcohol, and ether. It is of pale yellow color and is insoluble in any menstruum which does not act on it chemically. When boiled with strong hydrochloric acid and stannous chloride, leucine (30 to 40 per cent) and a small quantity of tyrosin (0.25 per cent) are found among the products of its decomposition, together with ammonia, glycine, and aminovalerianic acid, but not aspartic or glutamic acid. This behavior distinguishes elastin from both proteids and gelatin, since the former yield aspartic and glutamic acids but no glycine, while gelatin never yields a trace of tyrosin. Elastin is digested by the body enzymes. It is allied to the fibroin of silk and spider web.

Quite independently J. A. Wilson[4] has shown definitely that the elastin of the skin is removed by the tryptic enzymes of the bate. In the unbated skin the elastin fibers are fairly dense in the grain layer. As the bating proceeds, they gradually disappear, and at the end of 24 hrs. the grain is quite free from elastin. In skin delimed with ammonium chloride only, the elastin was left apparently unaltered. Wilson concludes that the mechanism of bating consists of two distinct parts: (1) reducing the limed skin to a condition of minimum swelling, and (2) digesting the elastin fibers present in the outer layers of the skin. It may be added that Mr. Seymour-Jones considers the so-called hyaline layer to be really the deepest layer of the epithelium, and proposes to call it the grain membrane, as being more in harmony with the nomenclature of the leather industry. In light leather manufacture it is what is called a "flywing" and yields practically no gelatin on boiling, whereas the split flesh is wholly transformed into gelatin.

Although the elastin is completely removed from the skins bated by trypsin for a sufficiently long time, about 24 hrs., in practice the bating is not continued to this point, but is carried on for only about 2 to 6 hrs. The elastin is only partly removed in this time, but the skins make good leather. The writer believes that it is not necessary, or even desirable, for the whole of the elastin to be removed or dissolved in order to let the skin down, but that it is sufficient for the elastic fibers to be broken up or weakened, in order that the desired suppleness may be obtained.

There still remain many unsolved problems in the bating process; these are being pursued with vigor, and the writer looks forward confidently to the time when we shall be able to bate any kind of skin by means of artificial bates suitable to the particular leather required.

DRENCHING

In the manufacture of many kinds of light leathers, skins are drenched after bating. This process usually consists in placing the skins in a mixture of bran and water (5 to 10 g. per liter) at a temperature of 30° to 35°. This ferments vigorously for 18 to 24 hrs., with evolution of a considerable quantity of gas and the formation of weak organic acids. In a drench taken in actual work, the gases had the following composition:

	Per cent
Carbon dioxide	25.2
Hydrogen sulfide	Trace
Oxygen	2.5
Hydrogen	46.7
Nitrogen	26.0

The acids produced per liter were:

	Gram
Formic	0.0306
Acetic	0.2042
Butyric	0.0134
Lactic	0.7907

Of other bodies formed during drenching, the quantity is insignificant, trimethylamine being the chief. It has been shown that the starch of the bran is converted into glucoses and dextrin by the action of an amylolytic enzyme, cerealin, allied to diastase. This enzyme was discovered by Mege Mouries.[1] It resembles the diastase of translocation described by Brown and Morris[2] in their work on the germination of grass seeds. It transforms starch into dextrin and glucose, whereas ordinary malt diastase transforms starch into dextrin and maltose. The action of cerealin is much slower than that of diastase. Dr. W. H. Wilcox and the author found that in 12 hrs. at 40° about one-half the starch is transformed. With malt extract, the whole of the starch disappears in about 2 hrs. The glucoses are then fermented by bacteria (*Bacillus furfuris*) with the formation of the organic acids above mentioned. The principal acid produced is lactic; the acetic acid is produced directly from the glucoses without any preliminary alcoholic fermentation by yeasts.

The mode of action of the drench on the skins is as follows:

1—Solution of the last traces of lime not removed by the bate and the subsequent swelling action of the organic acids on the skin fibers. The acids also dissolve a small amount of skin substance.

2—Distension and floating of the skins by the gases produced by the fermentation.

3—Mechanical absorption of dirt by the particles of bran or flour in the drench.

---

[1] *Chem. World*, **1912**, 403.

[2] *J. Soc. Chem. Ind.*, **31** (1912), 1105.

[3] "Biochemical Studies of Skin," *J. Am. Leather Chem. Assoc.*, **11** (1916), 463.

[4] THIS JOURNAL, **12** (1920), 1087.

[1] *Compt. rend.*, **37** (1853), 351; **38** (1854), 505; **43** (1856), 1122; **48** (1859), 431; **50** (1860), 467.

[2] *J. Chem. Soc.*, **57** (1890), 458.

It will thus be seen that the action of enzymes in the drench is an indirect one.

Tan Liquors

In the tan liquors changes go on which are brought about by enzymes; some of these are secreted by molds and yeasts and others are present in the plants from which the tanning materials are extracted. Unfortunately very little is known about these enzymes, but attention should be called to the work of Fernbach[1] in France, who prepared an enzyme which he called tannase from the mold *Aspergillus niger*, obtained from gall nuts. He cultivated the mold in Raulin's liquid, using tannin in place of the sugar. The product was macerated in water, the maceration concentrated at a low temperature *in vacuo*, the liquid precipitated by alcohol, and the precipitate treated exactly as in Lintner's method for the preparation of amylase. The gray powder thus obtained, when dissolved in water, acted rapidly on tannin at 50°, converting it into gallic acid. The solution of tannase filtered through a Chamberland filter into a sterilized solution of tannin acted just as effectively, proving that the action was due to an enzyme and not to a fermentation through the agency of organized cells.

H. Poltevin[1] prepared a solution of tannase by a process similar to that of Fernbach, but independently of him. Along with the gallic acid formed there is also a variable amount of glucose in the case of commercial tannins, but he considers these commercial tannins as mixtures. From a purified tannin he obtained gallic acid corresponding to 98.5 per cent of the tannin. The fact that tannase also hydrolyzes phenyl and methyl salicylates lends support to Schiff's formula for tannin, $C_6H_2(OH)_3.COO.C_6H_2(OH)_2.COOH$. In nature tannin is often accompanied by gallic acid. No doubt the latter is formed by the action of tannase, which Poltevin found to exist in sumac leaves, and which no doubt occurs in other substances containing tannin.

A Critical Study of Bating[2,3]

By John Arthur Wilson and Guido Daub

Laboratories of A. F. Gallun & Sons Co., Milwaukee, Wisconsin

In an earlier paper[4] it was shown that the mechanism of bating limed skins in the tannery by means of pancreatin and ammonium chloride consists of two distinct parts: reducing the skins to a condition of minimum swelling, and digesting the elastin fibers which are present only in the outer layers of the skin. The progress of this digestion was shown by means of photomicrographs of cross sections of the skin taken at intervals during bating. The examination of more than 200 sections under the microscope failed to reveal any other function of the bating process, even when a great variety of stains was employed on the sections. It therefore would appear that the primary function of bating is the removal of elastin, since the skins may be brought to a condition of minimum swelling simply by regulating the hydrogen-ion concentration of the solution with which they are in contact and, furthermore, this condition is only a temporary one, while the removal of elastin is permanent. The work described in this paper was confined to a study of the removal of elastin from calfskin and its effects.

Preparation of Skin for Examination

The most reliable method we know for studying the progress of bating is by means of the microscope. The per cent of elastin removed by any treatment is estimated by observing under the microscope cross sections of the samples taken before and after the treatment. For this purpose the sections must be suitably prepared, and the following procedure has been found quite satisfactory. Strips of the sample, about 2 in. × 0.5 in., are dehydrated with alcohol and soaked successively in (1) a mixture of equal volumes of alcohol and xylene, (2) a mixture of 1 volume of melted phenol to 3 of xylene, (3) pure xylene, and (4) melted paraffin, after which they are imbedded in paraffin and sectioned at 40μ. The sections are then stained either by means of Weigert's stain as described by Gage[5] or by the following method which the writers have found convenient: The section is washed on a slide with xylene, then with the alcohol-xylene mixture, and finally with pure alcohol. The whole slide is covered with alcohol saturated with Bismarck brown and kept over night in an airtight jar containing alcohol. Next day the section is rinsed with alcohol, alcohol-xylene, phenol-xylene, and finally with pure xylene. A drop of Canada balsam and a cover glass are then put over the section, which is now ready for examination and may be kept indefinitely for record.

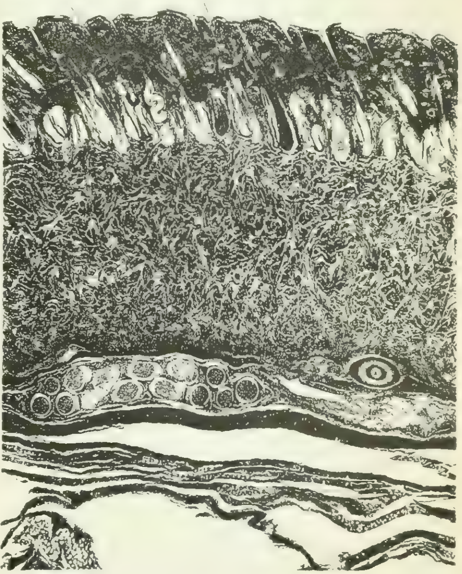


Fig. 1—Cross Section of Skin of Young Heifer Calf. Magnification, 25 Diameters

Fig. 1 is a photomicrograph of a cross section of the skin of a healthy young heifer calf. A strip from the butt was taken an hour after the death of the animal and fixed in Erlicki's fluid. A section was stained first with Weigert's stain and then with an alcoholic solution of picro-red. It was photo-

---

[1] *Compt. rend.*, **26** (1848), 1214; *J. Soc. Chem. Ind.*, **20** (1901), 137.

[2] Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[3] Received August 3, 1921.

[4] This Journal, **12** (1920), 1087.

[5] "The Microscope," **1917**, 355.

[1] *Compt. rend.*, **26** (1848), 1215; *J. Soc. Chem. Ind.*, **20** (1901), 137.

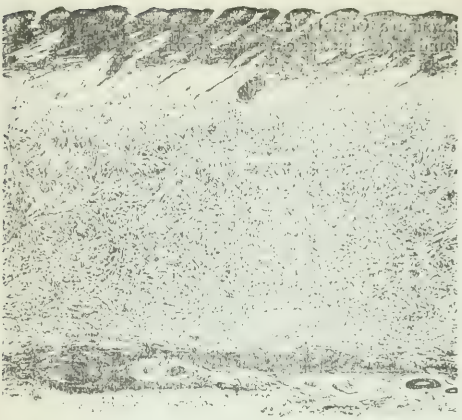


Fig. 2—Cross Section of Calfskin Taken after Fleshing, Liming, Unhairing, and Washing, before Bating. Magnification, 25 Diameters

graphed through a combination of Wratten filters B-2 (green) and E-2 (orange). The elastin fibers show as a dark layer about 0.4 mm. deep between the epidermis and hair roots. Other layers of elastin fibers are visible in the flesh, supporting the nerve bundles and fat cells.

Fig. 2 represents a section from the butt of a calfskin taken after fleshing, liming, unhairing, and washing, but before bating. The flesh, epidermis, and hair have been entirely removed, but the elastin fibers are still intact and show as dark layers near the upper and lower surfaces of the skin. The main body of the skin contains no elastin.

Fig. 3 represents a section from the same skin as that shown in Fig. 2, but was taken after bating. The elastin fibers have been completely digested by pancreatin. The sections shown in Figs. 2 and 3 were prepared and stained with alcoholic Bismarck brown exactly as described above. They were photographed through a Wratten filter H (blue-green).

Estimates of the per cent of elastin removed were made on the basis of removal from the grain layer only. In some cases all of the elastin was removed from the grain layer before half of it was removed from the flesh layer. Since the shaving operation removes practically all of the flesh elastin, its removal in bating is of little importance.

Materials Used

The chemicals employed were the ordinary C. P. variety. The enzyme was a commercial sample of U. S. P. pancreatin which showed by analysis: water, 6.3 per cent; insoluble matter, 40.0 per cent; ash, 6.8 per cent; N, 11.0 per cent; Cl, 1.7 per cent; SO_3, none; and P_2O_5, 3.5 per cent. By the method for determining tryptic activity described by Thomas,[1] 100 mg. of the sample acting upon 1 g. of casein in 100 cc. of solution for 1 hr. at 40° digested 64 mg. of nitrogen.

General Procedure

For each series of experiments a piece of limed and unhaired calfskin was cut into strips about 2 in. × 0.5 in. and thoroughly washed. There is a small, but appreciable, difference in time required for complete removal of elastin from skins of different thickness and for this reason great care was exercised in selecting all strips for any one series from the same part of the same skin, so as to have them all as nearly identical as possible. Each strip was put into 500 cc. of liquor, a volume large enough to prevent the skin from seriously altering the concentration of the liquor. The liquors were put into dark brown bottles to shield them from the light and were kept in a large Freas thermostat for the stated lengths of time at 40° ± 0.01°, the optimum temperature for most enzyme actions.[1]

Every liquor contained 0.02 mole per liter of added phosphoric acid to act as a buffer in addition to the enzyme and the KOH required to give the desired hydrogen-ion concentration. The hydrogen-ion concentration of each liquor was determined both before and after the digestion period by means of Hildebrand electrodes and a Leeds and Northrup potentiometer, excepting where it was proved by previous test that the results obtained by the Clark and Lubs series of indicators were sufficiently accurate. Except for the more strongly acid and alkaline solutions, the change in pH value during digestion was practically negligible.

As a rule, a preliminary series covering a very wide range was run, followed by a second series covering only the active range of the enzyme. A third series was usually run as a check.

Effect of Hydrogen-Ion Concentration

It is well known that the hydrogen-ion concentration is an important factor in determining the rate of digestion by enzymes. Using 0.1 g. of pancreatin per liter and digesting for 24 hrs., the writers obtained complete removal of elastin from the skin only between the pH values 7.5 and 8.5. A portion of the pancreatin was put into a collodion sac and dialyzed against running tap water in a dark room for 16 hrs. and used in a duplicate series in such quantity as to represent 0.1 g. per liter of the original pancreatin. The results were the same as those obtained with undialyzed enzyme. A series was then run in which the concentration of pancreatin was increased to 1.0 g. per liter. Complete removal of elastin was obtained between the pH values 5.5 and 8.5. The results of the two series, which are shown in Fig. 4, were carefully checked to insure their accuracy. The per cent of total elastin removed is plotted against the pH value of the solution taken after digestion and cooling to 25°.

The peculiar relation of the curves to each other is significant. They nearly coincide at all pH values above 7.5, but at 6.0 the stronger solution is still at its optimum activity, while the weaker one has apparently entirely lost

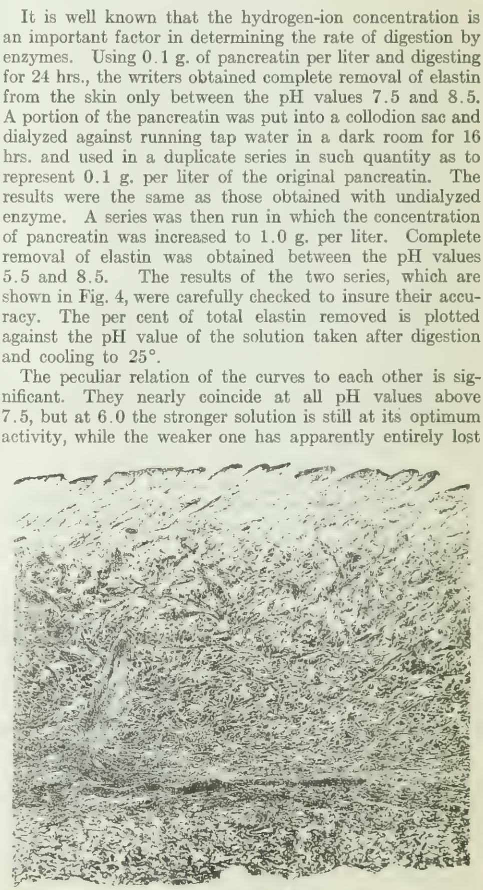


Fig. 3—Cross Section of Calfskin Taken after Bating. Magnification, 25 Diameters

---

[1] *J. Am. Leather Chem. Assoc.*, **15** (1920), 221.

[1] Falk, "The Chemistry of Enzyme Actions," **1921**, 77.

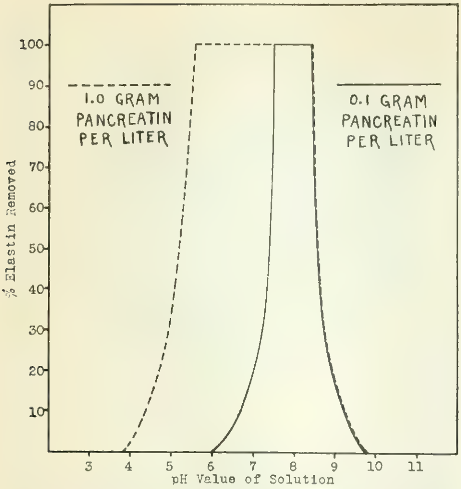


Fig. 4—Removal of Elastin Fibers from Limed Calfskin as a Function of Hydrogen-Ion Concentration. Time of Digestion 24 Hrs.; Temperature 40° C.

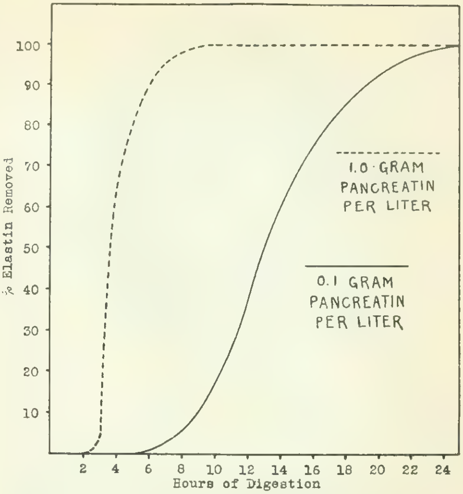


Fig 5—Removal of Elastin Fibers from Limed Calfskin as a Function of Time of Digestion. Temperature 40°; pH Value 7.6

its elastin-digesting powers. When an enzyme has been found to have different optimum pH values with different substrates, it has been supposed that the effect of the hydrogen-ion concentration upon the substrate has been the determining factor. But here we have the same enzyme and the same substrate, with a change in the optimum range due merely to a change in concentration of the enzyme.

An explanation is suggested by the recent work of Northrop,[1] who has shown that the activity of an enzyme solution is not necessarily a function of the apparent total enzyme concentration, but that a portion of the enzyme may be inactivated by combining with peptone or other foreign matter. He has pointed out further that the extent of the formation of addition compounds between protein and enzyme depends upon the concentration of protein ion, which is in turn a function of the hydrogen-ion concentration. If some protein other than elastin is responsible for the inactivation of a portion of the enzyme, we should expect such action to be a minimum at the isoelectric point of this protein.

After bating, the strips of calfskin were all carefully examined for the "bated feel," which apparently bears no relation to elastin removal, but corresponds to a condition of minimum swelling of the skin. The only strips passing this test were those from liquors having pH values between 6.10 and 9.80, suggesting that the isoelectric point of at least one of the skin proteins lies between these points. The average of these is 8, which is also the midpoint of the optimum range for the more dilute enzyme solution.

The following explanation is therefore not an improbable one: At a pH value of about 8, practically all of the enzyme is left free to attack the elastin, but as the pH value is decreased and the concentration of protein ion correspondingly increased, more and more enzyme is removed from the field of action by combining with it. In the weaker solution at pH = 6.0 practically all of the enzyme is in combination with this protein, whereas in the stronger solution the excess of enzyme is still sufficient to digest elastin. In dealing with the effect of hydrogen-ion concentration upon enzyme action, it is evidently important to know the effect of the hydrogen-ion concentration upon each substance in contact with the solution.

It is interesting to compare the optimum pH values for tryptic digestion found by other investigators:[1] for albumose Michaelis and Davidsohn[2] found 7.7, for casein Sherman and Neun[3] found 8.3, while Long and Hull[4] found 5.5 to 6.3, and for fibrin Long and Hull[4] found 7.5 to 8.3. The total range of 5.5 to 8.3 corresponds closely to the range found by the present authors, 5.5 to 8.5, for complete removal of elastin by the more concentrated enzyme solution.

At pH values less than 3.0 there was a marked destruction of the collagen fibers, possibly due to acid hydrolysis, and the strips were much swollen and rubbery, but no removal of elastin could be detected.

Effect of Time of Digestion

Two series of solutions were prepared, one in which the concentration of enzyme was 0.1 g. per liter and the other in which it was 1.0. All members of both series were otherwise identical. The pH value of each liquor was brought to 7.6 and this did not change during digestion. Each strip of calfskin was kept in a separate bottle. The bottles were removed from the thermostat at fixed intervals during 24 hrs.

Complete removal of the elastin was effected by the stronger enzyme solution in 6 to 8 hrs., but in the weaker solution 24 hrs. were required. The progress of the digestion is shown in Fig. 5. The time required to start digestion, 2 hrs. for the stronger and 5 hrs. for the weaker solution, was apparently the time required for the enzyme to diffuse into the region of the skin containing the elastin fibers. As will be seen from Fig. 2, these begin about 0.1 mm. below the grain surface.

Effect of Concentration of Enzyme

Two identical series of solutions were prepared in which the individual members differed only in concentration of pancreatin. The pH value was fixed at 7.6. One series was kept in the thermostat for 5 hrs. and the other for 24 hrs. The results are shown in Fig. 6 and furnish a study in economy.

---

[1] *J. Gen. Physiol.*, **2** (1920), 471; **3**, 211.

[1] Cf. Falk, *Loc. cit.*, p. 66.

[2] *Biochem. Z.*, **36** (1911), 280.

[3] *J. Am. Chem. Soc.*, **38** (1916), 2203; **40** (1918), 1138

[4] *Ibid.*, **39** (1917), 1051.

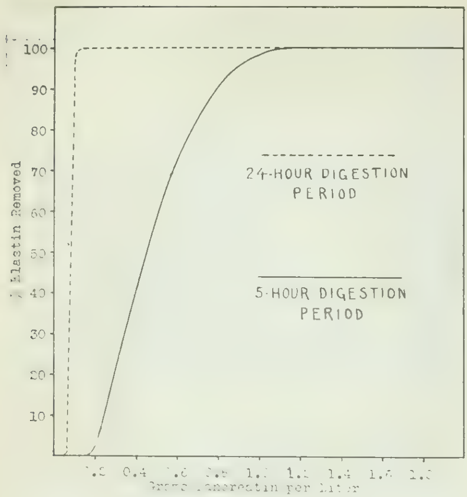


Fig. 6—Removal of Elastin Fibers from Limed Calfskin as a Function of Concentration of Enzyme. Temperature 40°; pH Value 7.6

Complete removal of elastin is effected by 0.1 g. of pancreatin in 24 hrs. or by 1.1 g. in 5 hrs.

Effect of Concentration of Ammonium Chloride

A study of bating would not be complete if it did not include the effect of ammonium chloride, one of the most abundant constituents of commercial bating materials. Aside from its use as a filler, it has been assumed to be beneficial in removing lime from the skins and tending to maintain a slight alkalinity favorable to tryptic digestion.

In this experiment two series of solutions were prepared in which the concentration of enzyme was 0.1 and 1.0 g. per liter, respectively. To each successive member of each series increasing amounts of ammonium chloride were added and the pH values of all members brought to 7.6. The time of digestion was 24 hrs. (Fig. 7).

In working with very dilute enzyme solutions, a distinct activating effect was noted upon the addition of 0.5 g. per liter of ammonium chloride, while larger amounts showed an inhibitory effect. With thin calfskin the activating effect was not detectable with the solution containing 0.1 g. per liter of enzyme after a 24-hr. digestion period, because all of the elastin was removed without adding any ammonium chloride. In order to show the activating effect in these experiments, strips from heavier skins were used, which require a somewhat longer time for complete removal of elastin under fixed conditions. The activating effect of 0.5 g. of ammonium chloride per liter and the inhibitory effect of greater concentrations are very marked. It is also interesting to note that the effect of ammonium chloride can be entirely overcome by a sufficient excess of enzyme.

This behavior of ammonium chloride is interesting in view of the finding of Thomas[1] that potassium bromide in concentrations of 0.0 to 0.1 mole per liter has an inhibitory effect upon the action of malt amylase, but in greater concentration has an activating effect.

At concentrations greater than 50 g. per liter the ammonium chloride exerted a destructive action upon the collagen fibers, possibly due to the formation of ammonia.

It is not our purpose to discuss the merits of commercial bates, but the question naturally arises as to what is the effect of the large amount of ammonium chloride which they contain. A sample which we believe contained pancreatin was found to have no elastin-digesting power at any concentration. It was our first thought that the trouble was due to too high a ratio of ammonium chloride to enzyme, but the preparation was still quite without action after the salt had been removed by dialysis. The real cause may have been the presence of much woody fiber used as a filler. If protein can remove the enzyme from the field of action, it is possible that woody fibers can also and, if these have an isoelectric point much removed from that of the protein, it is possible that at any concentration or at any pH value, a greater proportion of enzyme to woody fiber would be required than the sample contained.

Effect of Elastin Removal

A limed calfskin was cut into halves along the line of the backbone, the elastin was completely removed from one half by means of pancreatin, while the other half was simply treated with dilute ammonium chloride solution having a pH value of 8 in order to reduce its swelling to a minimum. Both halves were then thoroughly washed. It was recognized that an exact comparison of the two halves during tanning could not be made, if the pH values of the absorbed water were very different. Every effort was made to have the pieces identical, excepting for elastin content.

The most noticeable difference was observed during the early stage of vegetable tanning. The surface layers of the skin naturally tan more rapidly than the fibers in the interior and there is a tendency for the grain surface to expand temporarily to a greater extent than the rest of the skin. The elastin fibers in the unbated half evidently tended to prevent this expansion and the result of the tension produced was a slightly harsh feel, although the grain appeared tight and smooth to the eye. The grain of the completely bated half, however, actually expanded, giving the skin temporarily a wrinkled appearance, although the grain felt very soft and silky. When both halves had become completely tanned, this difference had almost disappeared. In the finished leather, the only difference in appearance was a slightly lighter color in the bated half. Photomicrographs

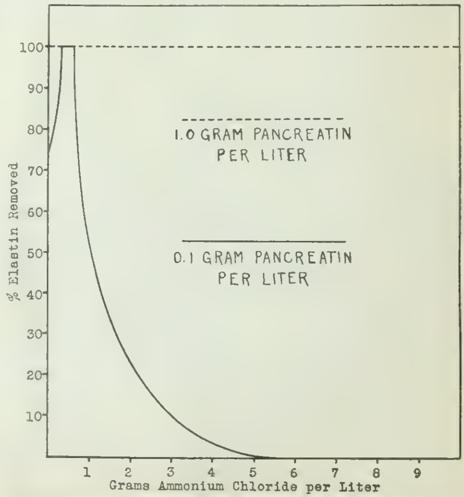


Fig. 7—Removal of Elastin Fibers from Limed Calfskin as a Function of the Concentration of Ammonium Chloride. Time of Digestion 24 Hrs.; Temperature 40°; pH Value 7.6

---

[1] *J. Am. Chem. Soc.*, **39** (1917), 1501.

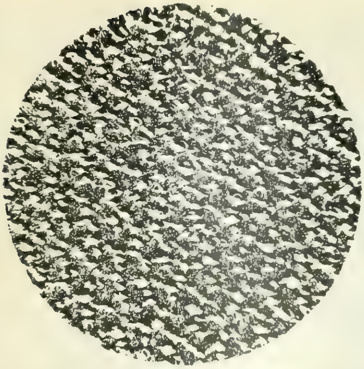


Fig. 8—Grain Surface of Finished Calf Leather with None of Its Elastin Removed. Magnification, 15 Diameters

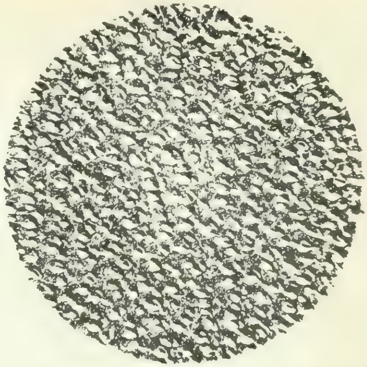


Fig. 9—Grain Surface of Finished Calf Leather from Which Elastin Has Been Entirely Removed. Magnification, 15 Diameters

of exactly corresponding points on the grain surface of the two halves are shown in Figs. 8 and 9.

While bated and unbated finished leathers appear much alike to the eye, there are perceptible physical differences such as one might expect to find in view of the fact that the elastin fibers have been removed from under the grain of the bated leather. The desirability of completely, or even partially, removing elastin from skin depends upon the use to which the leather is to be put.

Summary

A critical study of bating has been made which tends to elevate a heretofore mysterious process to a scientific plane.

The primary function of bating is to remove elastin fibers from the skin prior to tanning.

When a dilute solution of pancreatin was employed, complete digestion of the elastin was effected only when the pH value of the solution lay between 7.5 and 8.5, but when a more concentrated solution was used, the range was extended to 5.5 and 8.5. An explanation of this is given on the assumption that an addition compound between the enzyme and protein other than elastin is formed in increasing amounts as the pH value is reduced from 8.

The rate of removal of elastin from calfskin is shown as a function of the concentration of enzyme and of the time of digestion.

Ammonium chloride shows an activating effect in concentrations up to 0.5 g. per liter and a marked inhibitory effect in higher concentrations.

The failure of commercial bates to remove elastin from calfskin is attributed to the presence of woody fibers.

A comparison of bated and unbated leathers is made.

……

NOTE: Since submitting this paper for publication, we have received an interesting communication from L. Krall of Geneva, Switzerland, bearing upon the subject. Having just seen the German translation of our first paper, he has written to claim priority in discovering, by means of the microscope, that the chief function of bating is the removal of elastin fibers from the skin. His experiments, performed at the University of Geneva from 1914 to 1916, proved that the elastin fibers of skin can be entirely removed by digestion in an infusion of dog dung at 40°. His photomicrographs show that the action of dung is practically identical with the action we found for pancreatin, thus furnishing further evidence of the soundness of Wood's conclusion that pancreatin is the active constituent of dung in bating. We did no experimenting with dung. Krall's important paper was unfortunately buried in a private bulletin published by the *Société Anonyme, anc. B. Siegfried,* of Zofingue, Switzerland, in June 1918, and we were not aware of its existence until his communication was received.

Cider Preservatives[1]

By R. D. Scott and E. G. Will

State Department of Health, Columbus, Ohio

The alcoholic content of cider having become of some importance with the advent of the Eighteenth Amendment, the need exists for an efficient preservative, both to prevent fermentation of fresh cider and for court work, to hold the alcoholic percentage of seized samples unchanged pending analysis.

Sodium sulfite, sodium benzoate, and salicylic acid are known to be used commercially for preserving cider, but no literature concerning any except sodium benzoate could be found. Accordingly, the following experimental work was undertaken.

Experiments on Fresh Cider

The cider used was prepared by the writers from reasonably sound, unwashed, and unpared apples, of which ten varieties were used. From this stock, 400-cc. portions were transferred to 500-cc. flasks which were loosely stoppered after the addition of the preservatives, and were placed in a dark cupboard. Both alcoholic and acetic fermentation would probably be more rapid under such conditions than if barrel lots had been used, thus subjecting the preservatives to more rigorous tests than might be the case in practice. Alcohol (per cent by volume) and acidity (g. per 100 cc. as acetic) were determined at intervals of 2 wks., 2 mo., and 6 mo. The room temperature during this period ranged from 18° to 25° C. Results after 6 mo. only are recorded in Table I, in which Samples 1 to 11 and Control A represent one lot of juice; Samples 12 to 18 and Control B, a different lot of juice, expressed 1 wk. later from the same lot of apples.

RESULTS—Saccharin, formaldehyde, sodium hypochlorite, and β-naphthol were not effective in preventing alcoholic fermentation when used in amounts up to 0.1 per cent.

---

[1] Received August 1, 1921.

TABLE I—RESULT 6 MO. AFTER ADDITION OF PRESERVATIVES TO FRESH CIDER

SAMPLE	PRESERVATIVE	Amount Added Per cent	Alcohol	Acidity
1	Sodium sulfite	0.10	0	5.18
		0.20	6.40	0.30
2	Boric acid	0.10	1.70	3.26
		0.20	3.44	0.32
3	Borax	0.10	0	4.76
		0.20	4.69	0.82
4	β-Naphthol	0.10	0.84	5.14
5	Chlorazene	0.01	0	5.94
		0.10	0	0.98
6	Sodium hypochlorite[1]	0.01	0	1.06
		0.10	4.90	0.35
7	Sodium benzoate	0.02	0	0.96
		0.04	0	1.08
		0.07	0	1.12
		0.10	0	2.66
		0.20	0	1.06
8	Salicylic acid[2]	0.07	0	3.71
		0.10	5.62	0.38
		0.20	0	0.43
9	Sodium fluoride	0.04	4.18	0.42
		0.07	0	0.28
		0.10	0	0.30
10	Thymol	0.04	0	1.06
		0.07	0	0.40
		0.10	0	0.40
11	Mercuric chloride	0.025	0	0.44
		0.05	0	0.50
		0.10	0	0.48
Control A	None	....	6.50[6]	0.40[7]
				5.30[8]
12	Resorcinol	0.10	6.48	0.78
		0.20	6.70	0.84
13	Salol	0.10	5.92	0.98
		0.20	5.91	0.98
14	Saccharin	0.05	6.15	0.94
		0.10	6.28	0.85
15	Formaldehyde[3]	0.05	0.15	1.44
		0.10	3.85	0.66
16	Sodium hydroxide	0.50	0	1.18
17	Hydrogen peroxide[4]	0.10	0	3.41
		0.20	0	0.24
18	Copper sulfate[5]	0.005	3.38	0.90
		0.01	0	1.20
Control B	None	....	7.50[6]	0.41[7]
				3.60[8]

[1] As available chlorine.
[2] Acidity is corrected for amount of salicylic acid present.
[3] As 40 per cent solution.
[4] As 3 per cent solution.
[5] As copper.
[6] Maximum.
[7] Initial.
[8] Final.

Sodium sulfite, borax, boric acid, resorcinol, and salol were not effective in amounts of 0.2 per cent. Sodium hydroxide (0.5 per cent), hydrogen peroxide solution (0.1 per cent), chlorazene (0.1 per cent), and copper sulfate (0.01 per cent as metal) checked alcoholic, but did not prevent considerable acetic, fermentation. As, in our opinion, all the above substances would have to be effective in smaller amounts than recorded to be of much value as preservatives, no further study of them was made. Mercuric chloride (0.025 per cent), thymol (0.07 per cent), and sodium fluoride (0.07 per cent) were effective in preventing both alcoholic and acetic fermentation.

Sodium benzoate in amounts as low as 0.02 per cent prevented any appreciable amount of alcohol from forming, not more than 0.1 per cent being present at any period, but even when used to the extent of 0.2 per cent did not prevent acetic fermentation. Gore[1] records similar results for sodium benzoate.

Salicylic acid (0.2 per cent) was effective in preventing alcoholic and acetic fermentations, but was not effective in 0.1 per cent strength. It may be noted that certain preservatives, in sufficient concentration, did not prevent complete alcoholic fermentation, but retarded or prevented acetic fermentation. It is also a point of interest that samples treated with boric acid and with borax developed a strong odor of ethyl acetate. The volatile ester content of the sample containing 0.2 per cent boric acid was found to be 0.86 g. per 100 cc., calculated as ethyl acetate.

EXPERIMENTS ON PARTLY FERMENTED CIDER

Tests were made to determine also the effect of preservatives when added to partly fermented cider. In one set the cider had stood for 3 days and contained 0.22 per cent alcohol, and in a second set it had been allowed to stand for 12 days and contained 3.00 per cent. Two stocks of juices were used, expressed from the same lot of apples, but at different dates. Control A represents the juice containing 0.22 per cent alcohol; Control B, the juice containing 3.00 per cent. The result after 6 mo., which did not differ markedly from those at 2 mo., are shown in Table II.

TABLE II—RESULTS 6 MO. AFTER ADDITION OF PRESERVATIVES TO PARTLY FERMENTED CIDER

	Amount Added	Alcohol		Acidity
PRESERVATIVE	Per cent	Initial	Final	Final
Sodium fluoride	0.10	0.22	1.05	0.42
	0.20	0.22	0	0.48
Thymol	0.05	0.22	0	0.44
	0.10	0.22	0	0.44
	0.20	0.22	0	0.40
Sodium benzoate	0.10	0.22	0	1.12
	0.20	0.22	0	1.14
Salicylic acid[1]	0.05	0.22	2.82	1.33
	0.10	0.22	0	0.46
	0.20	0.22	0	0.41
Control A, none			5.93[2]	0.40[3]
				3.00[4]
Sodium fluoride	0.10	3.00	0.42	2.92
	0.20	3.00	0	3.10
Thymol	0.10	3.00	2.51	0.43
	0.20	3.00	2.82	0.44
Sodium benzoate	0.10	3.00	0	2.84
	0.20	3.00	0	3.08
Salicylic acid[1]	0.10	3.00	0	3.20
	0.20	2.00	2.32	0.42
Control B, none			7.72[2]	0.52
				4.80

[1] Acidity is corrected for amount of salicylic acid present.
[2] Maximum.
[3] Initial.
[4] Final.

In the case of the cider containing 0.22 per cent alcohol, 0.05 per cent of sodium benzoate prevented the formation of additional alcohol, but 0.2 per cent did not prevent acetic fermentation.

Sodium fluoride (0.2 per cent), salicylic acid (0.1 per cent), and thymol (0.05 per cent) were effective in preventing further fermentation.

In the case of the cider containing 3.00 per cent alcohol, neither sodium benzoate nor sodium fluoride (0.2 per cent) prevented the formation of acetic acid. Thymol (0.1 per cent) and salicylic acid (0.2 per cent) were effective in holding the alcohol nearly unchanged and in preventing acetic fermentation. It required more of a given preservative to prevent change in partly fermented than in fresh cider.

For the purpose of preserving samples for analysis, thymol, salicylic acid, and probably mercuric chloride are effective. The latter has the disadvantage of being poisonous; since the chemist who examines a liquor is usually called on to state whether it is palatable and fit for beverage purposes, its use is not to be recommended.

Thymol, while effective, has the slight objection that it comes over in the distillate even when the sample has been neutralized, thus necessitating a second distillation with an excess of alkali.

Salicylic acid is, in our opinion, the most satisfactory preservative for samples to be used in court work, 0.2 per cent being sufficient. It is not dangerous to taste samples containing this amount, none distils over from the neutralized sample, it may be obtained from any druggist, and the amount present in the sample may readily be ascertained.

As regards finding a satisfactory preservative for commercial purposes, our results are not particularly encouraging. The use of sodium benzoate has some official sanction, but while small amounts prevent any appreciable alcoholic fermentation, acetic fermentation proceeds practically un-checked. Nevertheless, it is a practical means of keeping cider below the 0.5 per cent alcoholic limit, and the beverage thus treated could be safely dispensed until too sour to be palatable. The addition of 0.05 per cent of the preservative to the fresh juice should be sufficient.

---

[1] U. S. Bureau of Chemistry, *Bulletin* **118**.

While salicylic acid is not considered more harmful than other preservatives,[1] it has not been received with much favor. It would probably have to be used to the extent of 0.1 per cent, an amount probably somewhat too high to be desirable from a physiological standpoint. However, it should be mentioned that tests described in the above reference show only a slight ill effect from the ingestion of 1 g. per day for 30 days.

Conclusions

1—Salicylic acid 0.2 per cent or thymol 0.1 per cent will preserve cider effectively for the purpose of court work.

2—For preserving cider commercially, sodium benzoate and salicylic acid are of some value.

A New Qualitative Test for Sucrose in the Presence of Glucose[2]

By Leon A. Congdon and Charles R. Stewart

Department of Chemistry, Syracuse University, Syracuse, New York

Comparatively few qualitative tests for sucrose in the presence of glucose have been developed, for attention has been directed more especially to their quantitative estimation. The determination of specific rotation or reducing power before and after inversion with hydrogen chloride or invertase has been of value in the past as a means of identification. In considering the specific rotation of mixtures of sucrose and glucose in a compound of unknown composition, we must not lose sight of the fact that foreign optically active substances would influence this value. In selecting the reduction method, it must be taken into account that there is a slight reduction of copper by sucrose in the presence of invert sugar.[3]

In the color reactions with phenols in presence of concentrated acid, used for the identification of sugars, the development of the color is said to be due to the formation of condensation products between the phenol derivatives and the decomposition products obtained from the sugar (humus substances, furfural, aldehydes, etc.). The most important phenol derivatives used for color reactions with sugars are α-naphthol, thymol, resorcinol, orcinol, naphthoresorcinol, and phloroglucinol.

The α-naphthol method described by Rapp and Reseinfelder[4] and others[5] is extremely delicate for sucrose solutions, but, according to C. A. Browne,[6] the deep violet coloration is also given by solutions of invert sugar. The tints given by other phenol derivatives vary from cherry-red to deep purple. The coloration which sucrose gives with morphine, codeine, aconitine, veratrine, and other alkaloids, in presence of sulfuric acid is also given by invert sugar, the same being true for the coloration given with ammonium molybdate[7] in presence of sulfuric acid.

C. Reichard[8] has suggested the use of sodium arsenate or tannic acid in the presence of hydrogen chloride for the detection of sucrose, but the value of this test is undetermined as yet. The work of Reichard upon the reactions of carbohydrates showed that, in the cold, sulfuric, nitric, or hydrochloric acid converted sugar into a pasty mass, which did not dry in the air. Carbonaceous matter produced by the sulfuric acid did not separate until the mixture was heated. The green coloration of copper sulfate in hydrochloric acid was retained much longer when sucrose was present, and it inhibited somewhat the precipitation produced by the acid when added to mercurous nitrate. In the presence of hydrochloric acid, sucrose yielded a dark green coloration with potassium bichromate, a blue with ammonium molybdate, and a brown which changed to violet with ammonium vanadate. No coloration was produced with sodium tungstate or titanic acid in the presence of sulfuric acid. Sodium arsenate and hydrochloric acid gave a rose-red coloration with sucrose. Of the colorations produced with organic bodies, the most marked was the red with tannic acid in the presence of hydrochloric acid. The author points out the value of this tannic acid test, the resorcinol color test, and the arsenic acid reaction for the detection of sucrose.

Wiley[1] has suggested a qualitative test for sucrose in the presence of glucose. The sugar is treated with cobaltous nitrate and potassium hydroxide, after dextrin or gums have been removed with alcohol. Sucrose will produce a permanent amethyst-blue color while glucose will give a turquoise blue, passing over to a light green. In a mixture of these two sugars, the color due to sucrose will predominate, if not less than 10 per cent of the sucrose is present.

To discover a new method for the qualitative detection of sucrose, a study of the action of various organic solvents upon glucose and sucrose was made.

Experimental

The substances tested were sucrose and glucose whose impurities were less than 1 per cent. The reagents used for extraction were *n*-amyl alcohol, benzene, toluene, *p*-xylene, carbon bisulfide, ligroin, carbon tetrachloride, acetic acid, acetone, and ethyl acetate. No work was done with methanol, ethyl alcohol, ether, and chloroform, since their action has been thoroughly investigated and it has been found that sucrose and glucose are *both* insoluble in ether and chloroform, soluble in varying degrees in ethyl alcohol, and insoluble in methanol. The solvents had been redistilled and only those portions which boiled at the temperatures given in the accompanying table were employed in the experiments. A known weight (1 g.) of the sugar was taken, and the volume of the solvents used was 100 cc.

Solvent	Boiling Point	Glucose	Sucrose
n-Amyl alcohol	137	Soluble	Soluble
Acetic acid	118	Soluble	Soluble
p-Xylene	138	Insoluble	Insoluble
Toluene	111	Insoluble	Insoluble
Ligroin	90	Insoluble	Insoluble
Benzene	80	Insoluble	Insoluble
Carbon tetrachloride	76	Insoluble	Insoluble
Carbon bisulfide	46	Insoluble	Insoluble
Acetone[1]	56	Soluble (variable)	Insoluble (variable)
Ethyl acetate	74	Soluble	Insoluble

[1] There is an appreciable variation in the amounts of glucose and sucrose extracted by acetone, the former being more soluble.

The dry sucrose and glucose were placed separately in filter paper extraction thimbles. An ordinary Soxhlet extraction tube with reflux condenser, cooled by running water, was used for extraction. A small Bunsen burner was used to bring the organic solvent to the boiling point, and to keep the solvent boiling until the experiment was completed.

---

[1] U. S. Bureau of Chemistry. *Bulletin* **8A**, II, 757.

[2] Received June 9, 1921.

[3] G. L. Spencer, "Handbook for Cane Sugar Manufacturers and Their Chemists," J. Wiley & Sons, **1912**, 91.

[4] *Deut. Zuckerind.*, **1892**, 538.

[5] *Monatsh.*, **6** (1885), 198, abstr. *J. Chem. Soc.*, **50** (1886), 923.

[6] "Handbook of Sugar Analysis," J. Wiley & Sons, **1912**, 681.

[7] *Bull. assoc. chim. sucr. dist.*, **27** (1909), No 3, 179; abstr. *Chem.-Ztg.*, **33** (1909), 538.

[8] *Pharm. Zentralhalle*, **51** (1910), 979; abstr. *J. Chem. Soc.*, **98** (1910), 1117; abstr. *Expt. Sta. Record*, **25**, No. 9, 801.

[1] "Principles and Practice of Agricultural Analysis," III, p. 189, The Chemical Publishing Co., **1908**.

The time of extraction was 5 hrs.

The results of these extractions are shown in the table, in which the terms soluble and insoluble are used to show whether or not extraction was possible.

As noted in the table, glucose is almost completely extracted by ethyl acetate while sucrose is but slightly affected. A run was made using equal parts of the glucose and sucrose, duplicating the results already given. Upon cooling the ethyl acetate solution of glucose, crystals of this substance were formed.

Further work is being done to determine the value of ethyl acetate in the quantitative estimation of mixtures of glucose and sucrose, and also on the use of this organic solvent for the actual preparation of crystalline glucose. It is also contemplated to include in this work, mixtures of other sugars, such as fructose and other less common sugars. The effect of traces of water on the solubility of the various sugars in ethyl acetate will also be investigated.

SUMMARY

1—Ethyl acetate may be used as a reagent for testing a dry mixture of glucose and sucrose by the extraction method, affording a new qualitative test for the separation of glucose and sucrose in mixtures.

2—Further work is being done to determine the value of ethyl acetate in the separation of glucose from other sugars, the separation of sucrose from fructose, etc., the use of ethyl acetate for the quantitative estimation of the sugars, the use of this solvent in the preparation of crystalline glucose, and the effect of traces of water on the solubility of the various sugars in ethyl acetate.

Potash Shales of Illinois[1]

By M. M. Austin with S. W. Parr

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Investigation of the potash shales of Illinois was taken up in 1917 in an effort to find values in the residues from certain shales which were under investigation in the laboratory of applied chemistry at the University of Illinois, with primary reference to the amount of oil to be obtained on destructive distillation. The shale from one region, Johnson County, yielded from 45 to 50 gal. of oil per ton and would therefore be of interest for its oil yield alone. Other shales which were of questionable value from the standpoint of oil yield might come into the field of possible technical utilization if other values could be discovered in them. This constituted a primary reason for examining all samples for other values, such as phosphorus and potash. The samples, eighteen in all, were furnished through the courtesy of the Illinois State Geological Survey. They came from localities widely distributed over the state. None of the samples contained phosphorus in more than a trace. Although the majority contained 2 or 3 per cent of potash (K_2O), which is normal for shale rock, two formations showed a potash content of from 5 to 5.8 per cent (K_2O). Of these latter two, the more important is a black carbonaceous shale which outcrops at frequent intervals over a distance of about 7 mi. in Union County. The other is a green sandy shale of entirely different character occurring in Lee County near Dixon, Ill.

POTASH SHALES IN CEMENT MANUFACTURE

From a study of the potash situation it would seem that one of the hopeful sources for a domestic supply resides in the recovery of potash as a by-product from the manufacture of cement. Even though the average shale used in the cement mix does not contain more than 1.5 to 2.5 per cent of potash (K_2O), the potential supply from this source would be very great, as a result of the tremendous tonnage of cement being produced.

The Illinois shales that we are here considering, instead of having an average potash content of 2 or even 2.5 per cent, have a content of 5 per cent. They compare, therefore, very favorably with the greensands of New Jersey.[2] The first question that naturally arises, therefore, relates to the suitability of these Illinois shales for the purpose of compounding a suitable cement mix.

Illinois shales of suitable composition for cement making, according to Bleininger,[3] are shown in Table I. For comparison, two of the high potash shales are shown in parallel columns.

TABLE I—COMPARISON OF ILLINOIS SHALES WITH REFERENCE TO THEIR CEMENT-MAKING PROPERTIES

CONSTITUENT	Average of 8 Illinois Shales (Bleininger)	—Illinois Potash Shales— Sample 1	—Illinois Potash Shales— Sample 2
SiO_2	61.56	53.8	55.0
Al_2O_3	16.12	17.7	16.3
Fe_2O_3	2.96	5.8[1]	6.0[1]
FeO	3.52	...	...
CaO	0.94	0.7	0.3
MgO	1.79	1.8	1.5
K_2O	2.90	5.0	4.9
Na_2O	0.82	0.5	0.4
Ignition loss	6.72	11.9	13.0

[1] Total iron calculated to Fe_2O_3.

Samples 1 and 2 are the black carbonaceous shale from Union County. It will be observed that, except in potash content, they vary but little in composition from the average of other shales which are said to be suitable for cement making. Their high potash content might be an advantage also in the formation of the clinker, since it would tend to lower the burning temperature.

Other factors which are important in evaluating these shales for cement-making purposes are as follows:

	Sample 1	Sample 2
Silica-alumina ratio	3.02	3.37
Inert mineral content	0.63	0.75
Sulfur	2.40	2.80

The silica-alumina ratio is in the most advantageous zone, and the inert mineral content is low. The sulfur occurs principally in microscopic form as pyrite.

In average American practice the raw mix will contain 0.7 to 1.0 per cent of K_2O. On the basis of 65 per cent recovery, which according to Huber and Reath[1] it seems reasonable to expect, there would result an average yield of 2.9 lbs. of potash per barrel of cement. On the same basis, the potash shales whose analyses are given in Table I should yield 5.4 lbs. per bbl.

One other region in the state has thus far supplied a shale with a high potash content, but its cement-making possibilities have not been determined. This shale, from Dixon, in Lee County, contains 5.8 per cent of potash. It is coarse-grained and friable. While its green color is suggestive of the greensands of the East, the geological character of the material is quite different, as will be shown later.

CONSTITUTION OF ILLINOIS POTASH SHALES

The shales from Union County are peculiar in that they contain a small percentage of oil, present in the free state. This has no industrial significance, but it adds to the other volatile constituents, such as water of hydration, so that the reduction in weight upon ignition, as shown in Table I, amounts to about 12.5 per cent of the raw material, and the potash content of the residue becomes 5.75 per cent. With the Dixon shale but little loss occurs on ignition, and the potash percentage is about the same in either the ignited or the raw state.

---

[1] Presented before the Division of Fertilizer Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Chem. Met. Eng.*, **22** (1920), 815.

[3] Illinois State Geological Survey, *Bulletin* **17** (1912).

[1] *Chem. Met. Eng.*, **16** (1917), 702.

ACTION OF SULFURIC ACID—No very simple or direct method was available for determining the form of combination in which the potash was held. One procedure consisted in digesting 1 g. of the sample with 25 cc. of concentrated sulfuric acid, heating until about half of the acid had been removed, diluting, filtering, washing, and igniting the residue, and analyzing it for total potash. The percentage of potash found was considered as being in some other than the feldspathic form.

By this procedure 62 per cent of the total potash was found to be removed from the Union County shales, while from the Dixon shale only about 15 per cent was removed, showing a marked difference in the chemical composition of the two shales. Further proof of this difference was desired. It is true that in the process of cement manufacture the potash would be equally recoverable in either case; but from any other standpoint differences in the ease with which the potash might be removed by chemical solvents, or concentrated into a form for more ready extraction, might make a wide difference in the value of the shales from the two sources.

It is not the purpose of this discussion to go into the details of the experiments to determine the chemical character of the potash-bearing constituents. The method of analysis suggests that the potash in the Dixon shale is chiefly or altogether feldspathic in combination, and that the major part, at least, of the potash in the Union County shale is in some combination more nearly resembling the glauconitic or greensand formations. These formations are considered as being potassium-iron silicates with an average potash content varying from 5 to 7 per cent K_2O.

MICROSCOPIC EXAMINATION—Thin sections for study under the microscope were prepared. No very positive information came from such studies. In general it seemed evident that the Union County shales had passed through extensive secondary decompositions and that the Dixon shales had not. Both types, however, even in the undisturbed condition of the deposits, had their ultimate particles in such a finely divided state as to render impossible their re-solution and study under the microscope.

TESTS WITH PLANTS—A third method of study into the probable type of composition was as follows: Accepting the generally conceded fact that potash in feldspathic combination is only slightly, if at all, available directly as plant food, further data on composition might be obtained from experiments to determine whether some of the potash in the Union County shales was directly available for plant use. Some foundation for this theory was already afforded by the fact that 62 per cent of the total potash was soluble in acid. If the Union County shales were treated with strong acid in such a manner as to remove all their acid-soluble potash, and if the residue with the remaining 38 per cent of potash (presumably in feldspathic combination) were submitted to plant action and found lacking in available potash, this would afford a still further proof in the chain of evidence as to the type of potash combination in the original shale.

It is not our purpose to go into the details of the results from these pot cultures, which were conducted by the Agronomy Department of the College of Agriculture, further than to correlate the results, so far as they have a bearing upon the composition of the shales.

In Table II there is shown the behavior of the various shale materials when applied to a peat soil deficient in potash. Buckwheat was selected as the plant most responsive to the varying treatments. An equivalent quantity of potash was added in each case, except to the check pots which, of course, contained no added potash in any form. Each pot was made up of 7 kg. of peat soil, 60 g. of pulverized limestone, and the various types of shale material, ground to pass a 100-mesh sieve, and in an amount that would carry into the soil mixture in each case a total potash content of 1.61 g. (K_2O).

TABLE II—COMPARATIVE STUDY OF BUCKWHEAT GROWTH, USING SHALE MATERIALS OF DIFFERENT COMPOSITION

No.	Description of Pots	Condition of Plants Six Weeks after Planting
1	Check pot using peat soil with insufficient potash	Poor growth
2	Peat soil as in 1, with Dixon shale	Poor growth, not distinguishable from No. 1
3	Peat soil as in 1, with Union County shale, less 62 per cent of potash by acid extraction	Poor growth, not different from Nos. 1 and 2
4	Peat soil as in 1, with Union County shale ignited	Excellent growth more dense and taller than Nos. 1, 2, or 3
5	Peat soil as in No. 1, with Union County shale, Sample 1 not ignited	Excellent growth, not distinguishable in density or vigor from No. 4
6	Peat soil as in 1, with Union County shale, Sample 2 not ignited	Excellent growth, equal in every respect to Nos. 4 and 5

BUCKWHEAT PLANTS GROWING ON PEAT SOIL TO WHICH VARIOUS SHALE MATERIALS HAVE BEEN ADDED

1—Check
2—Dixon shale
3—Union Co., acid-extracted
4—Union Co., ignited
5—Union Co., No. 1, not ignited
6—Union Co., No. 2, not ignited

This amount of potash represents the weight per acre that would be present in a normal soil which was deemed to have an adequate supply of that constituent. The results presented in the table are also clearly shown in the photographic reproduction.

Pot 1 is the check, with deficient potash. Pot 2 has the standard equivalent of 1.61 g. of K_2O added in the form present in the Dixon shale, and Pot 3 has the same addition in the form of acid-insoluble residue from the Union County shale. An examination of these three pots seems to warrant the conclusion that potash in any available form is lacking in each case. This, therefore, would seem to confirm the previous assumption that the potash present in Pots 2 and 3 is in the feldspathic form.

By further reference to Pots 4, 5, and 6, there is an equally obvious indication that in these pots potash is present in a form available for plant use; and since the only variable in the experiment is the acid-soluble constituent, it is evident that the potash utilized by the plant comes from this source.

Moreover, ignition or non-ignition of the shale does not affect the property of the potash so far as food availability is concerned. It would be of scientific interest, of course, to be able to say more definitely in what form was the potash combination here found. We have compared it thus far in the discussion to the greensands of the eastern United States which are true glauconites. The most that can be said of these shales is that they are glauconitic in type. They may have been originally a feldspathic deposition which has undergone secondary decomposition *in situ*. Indeed, the region has other striking examples of decomposition, for example, the very pure deposits of amorphous silica, found so abundantly in Union County, as well as some very pure kaolins.

So far as conformity to greensand or glauconitic conditions is concerned, there is every justification for such a classification, as may be seen from the following quotation,[1] indicating the geological conditions under which the true glauconites are supposed to have been formed:

> The organic matter transforms the iron into sulfide which may be oxidized to hydrate, sulfur being at the same time liberated. This sulfur would oxidize to sulfuric acid, which would decompose clay, setting free colloidal silica, aluminium being removed in solution. Thus, we have colloidal silica and hydrated iron in a state most suitable for their combination. The potash which is necessary to complete the composition of glauconite may be derived from the decomposed fragments of crystalline rocks like orthoclase or white mica.

Upon analysis of the shale for iron in the pyritic form by methods developed in this laboratory,[2] it appears that when the pyritic iron is deducted from the total iron of the shale there remains 3.8 per cent of iron available for combination with the 3.1 per cent of potash present in the acid-soluble form, an amount which approaches the ratio for glauconitic material with sufficient approximation to warrant the classification thus proposed, *viz.*, not true glauconite but glauconitic in type.

We have noted above that some free oil was found to be present in these black shales. It is interesting to speculate as to whether or not in this material, potash feldspar has changed over into shale in the ordinary way, but that the free oil present has prevented the removal of the more soluble materials by an excess of water.

Extraction and Concentration of the Potash

The peculiar character of these shales, which seem different from any potash material which the authors have found described in the literature, would seem to warrant a search for some direct method for the extraction of the potash. The facts already presented coupled with the results of other work that we have done preclude the possibility of finding a successful method. Only two-thirds of the total potash content of the rock can be extracted with acids under any conditions. The fine grain and uniform distribution of the potash-carrying constituent make it impossible to bring about any mechanical separation.

Conclusions

1—In at least two localities in Illinois, shales occur which contain 5 per cent or more of potash.

2—Shale outcropping in several places near Jonesboro, in Union County, which contains 5 per cent of potash would be suitable, so far as can be determined from its chemical composition and physical character, for use in the manufacture of portland cement.

3—By using this material in the manufacture of cement and by applying the known methods of potash recovery, a yield of 5.3 lbs. of potash per barrel of cement could be obtained.

4—The constitution of the southern Illinois shale is complex. The shale contains free oil, bituminous matter, pyrite, undecomposed potassium-bearing rock, feldspathic in character, and potassium-bearing material of the nature of glauconite or greensand.

5—Shale from Dixon, Lee County, contains 5.8 per cent of potash, which is held for the most part in a more stable condition than that in the southern Illinois shale.

6—Extraction of the potassium from shale of either the southern Illinois or the Dixon type by means of solid or liquid reagents would seem to be impracticable, because of the cost of leaching and recovering potash from material where it is present in such small amounts.

7—The plant availability of the potash in the southern Illinois shale is probably characteristic of all the material of this type outcropping in that locality.

8—That part of the potassium in the southern Illinois shale which is soluble in sulfuric acid is shown to be in a combination of the glauconite type.

9—In southern Illinois shale having a potash content of 5.0 per cent in the raw condition or 5.6 per cent when ignited, 62 per cent of the total potash is glauconitic in character and is available as plant food.

The Determination of "Strength" or Neutralizing Power of Acid Calcium Phosphates[3]

By W. E. Wadman

102 Lord Avenue, Bayonne, New Jersey

Acid calcium phosphate has been used for a number of years in leavening powders and self-raising flours. Its function is of course purely that of an acid to liberate carbonic acid gas from sodium bicarbonate, and its capacity to do this is a prime factor in determining its value.

Its neutralizing strength is usually stated in terms of sodium bicarbonate, that is, the number of parts of bicarbonate neutralized by 100 parts of the acid phosphate.

Simple as such a determination may at first sight appear, there is more or less controversy over this matter.

History of Controversy

Comparatively few chemists have had experience with the chemistry of acid phosphates. Such as have had this experience have generally been connected with one or another manufacturer in a highly competitive business, and it has come about that the question of how the "strength" of acid phosphates should be determined is no longer a purely scientific one but is a factor in competitive trade.

Extraordinarily little has been published on the subject of the analysis of acid phosphates. Apart from a paper by Chas. A. Catlin and one by the present writer, both published about twenty years ago,[1] hardly anything on the subject has appeared in chemical literature.

Acid calcium phosphate was originally prepared as a substitute for cream of tartar in leavening powders, and for this purpose its strength was adjusted (by the addition of starch) to equal that of cream of tartar, *viz.*, 100 parts to neutralize 44.6 parts of bicarbonate, or the strength or "titration" was made "45" and for many years this was the regular and established custom of the trade. There was little or no dispute as to the strength, and the regular method of determining such strength was the obvious one of direct titration with standard alkali.

Competitive conditions, however, led the manufacturers to seek selling levers by which to boost their particular makes. Color, physical condition, absence of "free acid," and other points were in turn duly exploited until some maker hit upon "strength." By leaving out some of the starch it was easy to offer goods of 50 strength. Goods of 55, 60, and higher strengths were successively offered to the trade, until eventually all starch was omitted and the present form of starchless

---

[1] W. B. Clarke, *J. Geol.*, **13** (1900), 509.

[2] A. R. Powell with S. W. Parr, University of Illinois Engineering Experiment Station, *Bulletin* **111** (1919).

[3] Received July [illegible], 1921.

[1] Catlin, *J. Anal. Chem.*, **4**, Part 4 (1890); Wadman, *J. Am. Chem. Soc.*, **16** (1894), 333.

acid phosphate became common. With the complete elimination of starch, no further increase of strength could be obtained. But the necessity remained of having some selling point over competitors, and there arose a number of fantastic methods of determining the "strength" of acid phosphates.

All such methods have two points in common: Without exception they studiously introduce conditions totally unlike those occurring in practice, when the material is used in the actual baking operation, and, also without exception, they give higher results than tests made as nearly as may be under baking conditions. All such departures from a simple titration, conducted as nearly as may be under the conditions of actual baking practice, are made solely for the purpose of allowing the analyst to record higher "strengths." At any rate, the writer has yet to learn of any method being advocated that yielded lower results than simple, direct titration.

Chemical Considerations

At first glance it would seem impossible that there could be any great uncertainty in determining the acid strength of an acid substance. With cream of tartar, for instance, only one reaction is possible and the result is practically the same, no matter how varied the conditions of analysis as to dilution, temperature, direct or indirect titration, amount of indicator present, etc.

Phosphoric acid, however, admits of considerable variation in result, depending on the conditions of manipulation. The end-product may be either a di- or triphosphate (R_2HPO_4 or R_3PO_4), or it may be something between these two.

Normally, phosphoric acid tends to give a dibasic salt when neutralized by alkalies, and salts of this type are by far the most common. While the salts of the R_2HPO_4 form are still, strictly speaking, "acid" salts, in that there is still one atom of basic hydrogen present, they are not acidic in character but rather slightly alkaline, and will not displace carbonic acid from carbonates except under conditions far removed from those of the baking process. There are of course a number of tribasic phosphates, but in most cases special pains must be taken to bring about their formation. The third molecule of base is generally very feebly combined and often behaves (as in the trialkali phosphates) practically like a free base.

Acid calcium phosphates when neutralized tend to form mostly dicalcium phosphate, or possibly an intermediate between di- and tricalcium salt, but nearer the dibasic salt.

The basicity of the end-products can, however, be increased by various expedients, all more or less drastic, and differing from the conditions obtaining in actual use, and the measure of the increase in basicity of end-products is roughly proportional to the degree of difference.

Favorite methods to obtain this end are titration under excessive dilution, indirect titration using a large excess of alkali and boiling in the presence of this excess of caustic alkali, excessive heating, addition of foreign salts, etc. Very helpful to some of these methods is the fact that calcium phosphate goes down as a semigelatinous precipitate which adsorbs the indicator and inhibits the appearance of the color reaction unless considerable indicator is present. By using a very small amount of indicator (phenolphthalein) it is possible to obtain a very alkaline solution that is practically colorless.

Normal Conditions for the Determination

The real purpose of a strength test is to ascertain how much sodium bicarbonate can be neutralized (and its carbonic acid gas liberated) by a given weight of calcium acid phosphate, *when used in leavening breadstuffs*.

Such a test should therefore be conducted under conditions as nearly as possible like those prevailing in the practical operation of baking.

Some of these conditions are very lucidly set forth by Catlin in the paper referred to and there are one or two others that we may consider, which are never widely departed from in the practical baking operation.

1—Acid phosphate and sodium bicarbonate are simultaneously present in equivalent or approximately equivalent quantities. There is *never* the condition of an excess of sodium hydroxide. Hence, indirect titration wherein a considerable excess of sodium hydroxide is added and boiled with the assay brings about an entirely abnormal condition, tending to produce more basic end-products than simple neutralization.

2—Catlin has shown that in practical baking each gram of acid phosphate has available for reaction purposes about 45 cc. of water as a maximum and probably actually considerably less. Hence excessive dilution is an abnormal condition, nor should such excessive dilution be brought about indirectly by the expedient of using extremely dilute standard solutions. The end-point is at best vague, and there is no excuse for using anything weaker than 0.5 or 0.3 *N* solutions.

3—Catlin has shown that in practical baking, exposure to a boiling temperature (100° C.) lasts for about 1 min. only. Therefore if boiling is employed at all it should not last over 1 min., and of course in no case should it ever occur in the presence of an excess of caustic soda.

4—Apart from the mineral constituents of the flour no salts are present in practical baking other than the acid phosphate and the bicarbonate, except a small amount of common salt. Hence it is quite inadmissible to add to the assay any substance other than the standard alkali solution (and indicator) unless it be common salt in amount not exceeding one-half of the weight of phosphate under assay. One proposed method calls for the use of an enormous excess of common salt in the assay, which is, of course, inexcusable.

These conditions of actual baking practice can hardly be disputed. How can they be most nearly approximated in an analytical method? In the writer's opinion they are more nearly met by simple, direct titration, using about 30 cc. of water per g. of acid phosphate and employing standard alkali of approximately 0.5 *N* strength so as to avoid excessive dilution.

The major part of the alkali should be added quickly, but with vigorous stirring to prevent occlusion in the precipitate. The indicator (phenolphthalein) should be present in *liberal* amount so that adsorption by the precipitate does not render the end reaction invisible.

It is hard to imagine that any chemist sincerely believes that a mixture of insoluble calcium phosphates and disodium phosphate which exhibits a markedly alkaline reaction to phenolphthalein is still capable of liberating carbonic acid from carbonates.

An Inaccurate Method

There was recently submitted to the writer a "Method for Determining the Neutralizing Value of Monocalcium Phosphate," said to be used by the chemists of the Agricultural Department of one of the states, and by a number of other chemists, and which "they had found to be the *best*." As it is somewhat typical it is worth reproducing verbatim.

> Weigh into a No. 3A casserole 0.8401 g. of phosphate. Add 25 cc. of cold water and stir. Then run in 90 cc. of 0.1 *N* caustic soda solution from buret, bring to boil and boil 1 min. Add one small drop of phenolphthalein and titrate back with 0.1 *N* hydrochloric acid solution. The amount of hydrochloric acid required to cause the pink of the phenolphthalein to just disappear taken from 90 cc. of alkali used gives the neutralizing value of the phosphate in terms of sodium bicarbonate and is expressed in units.
>
> *Extreme care must be exercised in the amount of indicator used. We have found the most satisfactory results by using one drop.* [The italics are the present writer's.]

It may safely be said that the above method is wrong wherever it is specific.

Without any desire to be captious in criticism, it is utterly absurd to weigh to the fourth place in such tests. The end-point is at best vague, and indeterminate within 0.2 cc. of 0.5 *N* alkali (the writer makes this statement after years of experience and possessing an eye perhaps more than ordinarily sensitive to color changes).

The dilution is about two and one-half times what would occur in baking practice, and the alkali used is more than 30 per cent in excess of the neutralizing power of the phosphate. The instructions are to boil the test at this extreme dilution and in the presence of the huge excess of caustic soda, both conditions that tend to the production of abnormally basic end-products.

But the real scientific gem of the method appears in the instruction to add "one small drop" of phenolphthalein. If a sample of acid phosphate be titrated, following the above method precisely, and if more phenolphthalein be added at the completion of the test, the assay will immediately turn dark red, indicating strong alkalinity, and very considerably more acid will be required to discharge the color again. In fact, if sufficient indicator be used, the final result will approach the simple direct titration, although still somewhat higher, owing to the abnormally basic condition brought about by boiling with excess of caustic solution.

Now there is no escape from the fact that a test conducted according to this method was really very strongly alkaline at the point taken as the end-point, and that this alkaline condition was not evident, simply because insufficient indicator was present, and this with deliberate intent to obtain what is rather naively described as "the most satisfactory" result. It is quite manifest that "most satisfactory" means "highest possible" and nothing else.

There is not the least sanction either in sense or science for the prescribed limitation of the amount of indicator, and there can be no doubt whatsoever that this method of determining the "strength" of acid phosphates gives results about 15 per cent in excess of the true neutralizing value.

If acid phosphates are used with the proportion of bicarbonate of soda as indicated by this test, the resulting products must be strongly alkaline. It is an undoubted fact that acid phosphates *are* used in practice in the proportions indicated, and usually without serious results. In fact, an alkaline condition in breadstuffs may be desirable under some circumstances. But the business of the chemist is solely to report the true neutralizing value of the sample, irrespective of what limiting proportions *may* be used without provoking actual disaster.

Cream of tartar will neutralize sodium bicarbonate in the ratio of 100 to 44.6. There is not the slightest doubt that fairly satisfactory bread can be made using cream of tartar on a basis of 100 to 50, but this would not in the least justify the chemist in reporting cream of tartar as having this neutralizing strength.

DETERMINATION OF CORRECT VALUE

The titration of phosphoric acid, especially in combination with calcium, is necessarily indefinite for several reasons. The end-products are amphoteric in their action on indicators; for instance, they will at one and the same time turn red litmus blue and blue litmus red. This phenomenon is probably a result of the tendency to hydrolysis, especially on dilution or heating, as, for instance

$$Na_2HPO_4 + 2H_2O \rightleftharpoons NaH_2PO_4 + NaOH.$$

Lastly, the end-products may be considerably more basic than dicalcium phosphate if suitable conditions are provided.

As might be expected, considerable work has been done in the attempt to prove conclusively what is the true working value of acid phosphates, and not a little of such work by the writer or under his direction. While he is entirely convinced as a result of his experience, he recognizes the extreme difficulty of furnishing apodictic proof.

A rather conclusive test, devised and worked out by Mr. A. L. Konwiser, formerly assistant to the writer, is perhaps best described by recounting the procedure of an actual series of tests.

A sample of acid phosphate gave a neutralizing value of 69.7 by direct titration. The same sample, titrated precisely in accordance with the "Agricultural Station Method" quoted above, gave a strength of 80+.

A mixture (baking powder) was prepared from C. P. cream of tartar and sodium bicarbonate in exact stoichiometrical proportions, *i. e.*, 100 to 44.65. This was designated as No. 1 and constituted a standard of neutrality or control. Similar mixtures were prepared with the acid phosphate and bicarbonate in the proportions of 100:70, 100:75, and 100:80, and numbered 2, 3, and 4, respectively. All these mixtures were weighed upon a chemical balance to insure accuracy.

Biscuits were made with the four powders, using only flour, water, the leavening powders, and salt. The biscuits were baked side by side in the same oven and when "done" were split open and spotted with specially purified and carefully neutralized litmus solution (purple).

The following results were observed:

SAMPLE	RESULTS
1	The purple color of the litmus was unchanged
2	Color purple but markedly bluer than Sample 1
3	Immediate full blue color. Alkaline
4	Same as Sample 3. No increase in blueness

The acid phosphate used on the 100 : 70 basis (that is practically the indication of the simple direct titration) yields a biscuit that, while very slightly alkaline as compared with the strictly neutral cream of tartar biscuit, is still, for all practical purposes, neutral.

The acid phosphate used on the 75 basis gives a completely alkaline reaction, and the intensity of the blue color is not increased when the acid is used on the 80 basis. In other words, the excess of soda on the basis of 75 is already so large that further excess does not change the color of the indicator.

The biscuits were submitted to a tasting test by an observer who knew nothing whatever of their make-up. This observer pronounced Nos. 3 and 4 "soapy" (that is, alkaline), and in the case of No. 4 the verdict was rendered with grimaces of distaste.

The final conclusion is that 70 (practically the indication of the simple direct titration) is about the correct working strength and is indeed at the upper limit at which it should be used; 75 is too high and gives an alkaline product, while 80 (the indication of the "Agricultural Station Method") is very much too high.

CONCLUSION

When one method of testing a substance gives results 15 per cent or more higher than another method, it naturally leads to embarrassing situations. As long as one manufacturer calls his product 75, 80, 85, or any other strength and can persuade his customers that he is correct, with or without the backing of chemists, official or other, his competitor must do likewise or lose business. But this does not appear to the writer to justify a chemist in reporting a neutralizing strength which he is perfectly sure is greatly in excess of the truth, nor can he salve his conscience by adopting methods that are manifestly devised for the purpose of giving high results.

The writer understands that an effort is on foot to bring about a standardization of the methods of testing acid phosphates—presumably a method sanctioned by the Association of Official Agricultural Chemists. In the very nature of the case absolute accuracy cannot be expected, but it is not difficult to outline a simple method, the indications of which, when applied in practice, will result in neutral or substantially neutral residues in food products.

The Determination of Moisture in Insulating Oils[1,2]

By C. J. Rodman

Research Department, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

Many methods of determining water in oils have appeared in the literature, but no reliable simple method has come to the author's notice. By examination of the literature in detail, a classification of methods has been made. This classification includes five qualitative, a dozen approximate, and few quantitative methods. In dealing with moisture in insulating oils, a method cannot be called quantitative unless an accuracy of closer than 0.002 per cent is obtained. The approximate methods include those which determine moisture content to an accuracy of 0.01 to 0.05 per cent. The qualitative tests are those which have been recommended here and there for the use of the electrical engineer as a rapid means of finding the presence of water. No insulating oil should be allowed to take up enough moisture to show positive tests by qualitative methods, because the dielectric strength of an oil becomes less considerably before the moisture can be thus detected.

Qualitative Tests

1—Addition of anhydrous $CuSO_4$. Turns blue with H_2O.[1,2] *

2—Hot nail "spits," indicating H_2O.[1,2]

3—Addition of certain water-soluble, but oil-insoluble dyes.[3]

4—Centrifugation.[1]

5—Electrical precipitation.[5]

Approximate Analysis

1—Loss of weight by heating. For nonvolatile oils and greases.[6,13]

2—Diluting with solvent and settling by gravity. Applicable to thin oils, but a diluent is to be avoided. Centrifugation may be used to hasten.[7]

3—Use of color comparator tube.[5]

4—Treating with normal acids.[6]

5—Treating with CaC_2. This is convenient, but with petroleums accurate to 3 per cent of the H_2O value only, as C_2H_2 is absorbed by them. The 3 per cent accuracy holds only above 0.01 per cent content.[8]

6—Treating with sodium. One cc. H_2 represents 0.0016 g. H_2O in the sample used. This is accurate and convenient. Complicated apparatus necessary to insure thorough contact of sodium with oil and to eliminate quantitatively all of the hydrogen.[6]

7—Distilling with a immiscible liquid. Water-saturated xylene, a mixture of xylene and toluene, or benzene and toluene are used. Accurate to approximately 0.033 g. of H_2O per 100 cc. of distillate.[6]

8—Directly distilling off the water. This is accurate to within 0.03 per cent, and does not apply to light oils.[6] Inert gases used to dry oils.[2]

9—Water in oils may be tested by conductivity providing no other decomposition products are present. Only approximate results obtainable.[9]

10—Oil mixture with organic solvent to produce cloud. A more general case than No. 7.

11—The Tyndall effect is used to determine finely divided water in suspension.

Quantitative Methods

1—By special application of No. 3 (qualitative tests) less than 0.003 per cent H_2O can be detected. Necessitates color scale, clear oils—standardization for quantitative work.

2—Vacuum treatment while shaking sample, heating, and collecting H_2O in P_2O_5 tube. Method quantitative if oil is free from nitrogenous volatile compounds, as is usually the case. By special method we are able to determine water to ±0.001 per cent.

3—Same treatment as No. 2, using freezing mixture to collect H_2O and volatile components, afterwards estimating water by No. 4 method. Good results obtainable, but complicated apparatus must be employed.

4—Vacuum treatment of thin film of oil running over heated surface. Vapor eliminated and measured by oil-water vapor pressure difference.

5—Mixing oil with dry ether (solvent), treating with CaC_2, drawing off C_2H_2 by vacuum, precipitating out in alcoholic $AgNO_3$ solution and noting change in resistance with precipitation of silver acetylide.[8] This gives time-rate curve and is very desirable where both hygroscopic and constitution moisture are involved. It is accurate to less than 0.01 per cent and is chiefly applicable to certain insulating materials and oils.

Inasmuch as the dielectric strength of an oil is greatly influenced by the moisture present,[10] it is highly desirable to determine the moisture content accurately. The different forms in which the moisture is present within the oil may vary greatly. This is dependent upon the composition of the oil and its impurities. Water may be in finely divided suspension, condensed nuclearly upon dust particles, absorbed by fibers or soaps, in colloidal form or in true solution. The true dielectric strength of pure oil is most strongly influenced by water in solution, but the usual conductivity takes place by the alignment of particles within the oil.

Very pure mineral oil of the paraffin series does not dissolve more than 3×10^{-4} per cent H_2O.[11] The unusually high percentage of moisture sometimes found in oils is attracted by impurities which are soluble in oil. Such impurities (unsaturated compounds, fatty acids, etc.) possess a greater coefficient of solubility for water than do the pure paraffins.

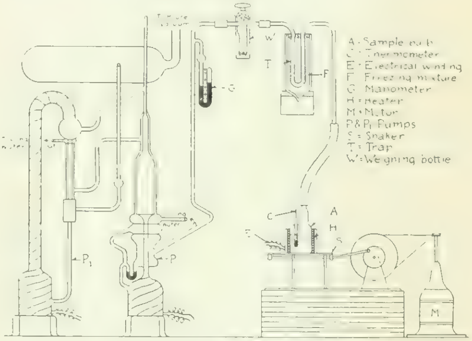


Fig. 1

Of the numerous possible methods of determination of water in transformer and similar oils only two or three may be depended upon for the accuracy desired. A modification of Method 2 (Quantitative Methods) has given excellent results.

Principle of Method

Water is fractionated from the oil at reduced pressure and elevated temperature, during rapid agitation of the sample. Under these conditions the partial pressures of oil and water are far apart and fractionation is rapid. The water is collected with some oil distillate in a trap cooled by liquid air. Redistillation of the water and collection in a P_2O_5 weighing bottle take place upon the removal of liquid air. The small amount of oil vapor distilling over passes on through the phosphorus pentoxide. The method depends for its success upon the production of a great number of thin films within the oil sample. A low freezing mixture may be substituted for the liquid air.

Apparatus and Procedure

Fig. 1 shows diagrammatically the arrangement of the apparatus. The weighing bulb* is of special design consisting of two glass parts, an inner and outer chamber. The inner chamber (2 cm. in diameter × 10 cm. long) is slightly constricted at the lower end and has a stopcock handle at the upper end. This fits concentrically within the outer chamber (2.5 cm. in diameter × 10 cm. long), and is made airtight by the ground joint near the top. An inlet allows gas to enter the outer chamber first. The gas passes downward through the outer chamber, entering the inner from the bottom. Pure P_2O_5 packed between two plugs of glass wool within the central chamber is used as the moisture absorbent. The gas passes up through the P_2O_5 and out through a small tube directly opposite the inlet. By turning the inner member through 90° the bulb is sealed to any gas pressure difference. Such a bulb holds a vacuum many weeks.

---

[1] Presented before the Section of Petroleum Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921

[2] Published as Scientific Paper 92 of the Westinghouse Electric and Manufacturing Company.

* Numbers refer to Bibliography.

* Modification of bulb used by Dr. H. C. P. Weber, Westinghouse Electric and Manufacturing Company.

The sample bulb, which fits within the heater shaker, is of about 50-cc. capacity. A tube, closed at the bottom and just large enough to accommodate a small thermometer (range 0° to 150° C.), passes down into the bulb. The bulb can be kept at any desired temperature by the electric heater surrounding it. The motor speed can be controlled so that the shaker runs from 50 to 250 per minute. The liquid air trap consists of a closely bent U-tube of 1-cm. tubing, surrounded by a Dewar flask containing liquid air.

PROCEDURE—Before making a run the apparatus is thoroughly cleaned and dried. A few cc. of oil to be tested are used to rinse the sample bulb before pipetting in the 25 to 40 cc. of the oil. The bulb is connected to the liquid air trap by means of a heavy, pure rubber, pressure tube. The P_2O_5 tube is fastened in place also by means of a rubber connection. Rubber cement prevents gas leakage at the joints. The vacuum is now turned on and the pressure very quickly reduced to a millimeter. The manometer reading is taken and the P_2O_5 bulb closed. Closing a screw pinchcock tightly at either connection to the P_2O_5 bulb suffices to hold the vacuum in the system when taking the P_2O_5 bulb out for weighing. The P_2O_5 bulb is replaced and screw cocks opened. While shaking and heating the bulb to 140° C. the liquid air trap is covered with CO_2 snow and acetone or liquid air contained in a silvered Dewar flask. The water vapor is quickly and completely eliminated from the oil and frozen in the trap, which also condenses any light oil distillate. Upon removing the freezing mixture the frozen water is rapidly vaporized and caught quantitatively within the P_2O_5 bulb. By closing the P_2O_5 bulb at the same pressure as in the blank weighing one can readily obtain the eliminated water by difference. Phosphorus pentoxide does not absorb any oil vapors at the pressures used.

Two methods of procedure may be followed. The more rapid method does not account entirely for the moisture in the air within any part of the apparatus. As shown in Table I, it gives comparatively good results, varying ±0.002 from the mean. A single determination is not to be recommended where the best accuracy is desired.

TABLE I

Water Added Per cent	Water Found Per cent	Difference
0.0042	0.0047	+0.0005
0.0194	0.0216	+0.0022
0.0110	0.0092	—0.0018
0.0088	0.0078	—0.001
0.0074	0.0086	+0.0012

$$\sqrt{d_1 + d_2, \text{etc.}} = 0.0012$$

In this case the vacuum is cracked without shaking the sample bottle, thus taking out the air above the oil sample when the weighing tube or freezing mixture is not yet in place. A pinchcock is immediately closed. The freezing mixture is then raised around the trap and the weighing tube put in place, and the determination is made as described above.

The second method of procedure takes into account the amount of moisture in the air. Two blank runs are first made to determine the humidity. Several runs made for humidity moisture check the theoretical values. With the addition of this correction to the first procedure, the moisture in hydrocarbon oils may be determined accurately.

NOTES ON THE METHOD

In determining the moisture content to ±0.001 care must be exercised at every point in the determination. The oil sample must be representative of that which is to be examined. Any apparatus used in connection with the oil should be carefully cleaned and dried and then rinsed with some of the oil sample. Humidity changes influence the water content appreciably if the sample is open to the air. Care should be exercised in keeping the breath away from the sample, as surface condensation of water vapor may greatly influence the result.* The time of a run should not exceed 20 min. This gives ample time to insure complete elimination of the moisture.

Factors which give high results, and hence are additive, may be briefly summarized as follows:

1—Surface condensation of water from humid air.
2—Contamination of any of the apparatus by water or dust.
3—Volatile nitrogenous and basic substances within the oil
4—External leaks of any kind.
5—Increase of pressure during run so that excess gas is trapped in P_2O_5 bulb.
6—Adsorption of some oil vapor in weighing bulb.

Subtractive errors are as follows:

1—Elimination of water not complete as a result of high viscosity of oil sample.
2—Bath temperature too low.
3—Shaking not vigorous enough to expose all the oil to thin film condition.
4—Decrease in pressure over the initial pressure within the bulb.
5—Time of shaking oil too brief.

Weighing errors may be positive or negative.

Using the representative transformer oil little difficulty is experienced in the determination of water due to its viscosity, impurities present, or to the volatility of the sample. Leaks are readily taken care of by using rubber cement between the glass-rubber connections. Other possible leaks are prevented by proper construction of apparatus. Freshly sublimed P_2O_5 free from organic matter will not absorb and hold any oil under low vacuum conditions. Should any oil distillate come over in appreciable quantities it is readily eliminated by surrounding the P_2O_5 tube by a temperature bath of 100° to 150° C.[12] Though the possible errors seem numerous, it is only necessary to recognize them to eliminate them by following out carefully the procedure recommended, and little difficulty will be experienced in obtaining an accurate result.

BIBLIOGRAPHY

1—*Elect. Club J.*, U. S. A., May **1904**.
2—*Elect.*, **66** (1911), 490.
3—A. H. Gill, "Oil Analysis," 6th Ed., **1913**, p. 22.
4—*Chem.-Ztg.*, **33** (1909), 1259.
5—Bureau of Mines, *Technical Paper* **25** (1912). See also patent literature.
6—*Orig. Com. 8th Intern. Congr. Applied Chem.*, **10**, 17.
7—*J. Ind. Eng. Chem.*, **10** (1918), 357; Direccion General de Mines, Buenos Aires, Bol. **3B** (1915).
8—U. S. Dept. Agriculture, Bureau of Chemistry, *Circular* **97**; *J. Soc. Chem.*, **29** (1910), 197; *Chem.-Ztg.*, **6** (1892), 29.
9—*J. Soc. Leather Chem.*, **3**, 101–4; **14**, 654–74; **3**, 206–8; *J. Ind. Eng. Chem.*, **12** (1920), 486–98
10—*Elect.*, **66**, 490; *Elect. J.*, **16**, 74–6.
11—See also *Elect.*, **82**, 103, 67, 818; *Z. anorg. Chem.*, **81**, 24–39; *Z. Elektrochem.*, **17**, 348.
12—*Z. anorg. Chem.*, **81**, 24–39.
13—*J. Soc. Chem. Ind.*, **39** (1920), 305.

---

* The rubber connections used in the vacuum line do not give up any appreciable amount of moisture after having been once subjected to low vacuum, if care is taken subsequently to keep out humid atmosphere.

A committee of eleven has been appointed to draft tentative plans for an organization of oil men, to comprise refiners, jobbers, producers, supply and tank men, which it is expected will embrace the entire oil industry of the southwest, probably with headquarters in Kansas City. Part of the plan includes the formation of an arbitration board to settle differences between conflicting interests, and an oil exposition to be held yearly.

Method for the Determination of Free and Combined Carbon Dioxide[1]

By **J. A. Shaw**

The Koppers Company Laboratory, Mellon Institute, Pittsburgh, Pa.

In the course of work on the analysis of mine water, it has been found that the ordinary titrimetric methods for the determination of carbon dioxide fail with acid waters. In fact, readings by the standard phenolphthalein method, when any reading is possible, give negative results, and in some cases this error is large. Considering also the fact that the titration of free carbon dioxide in alkaline waters leaves much to be desired, another means than the ordinary titration with alkali was sought.

Reference may be made here to the work of Swanson and Hulett[2] and of Van Slyke[3] and to the apparatus of Van Slyke for the determination of certain constituents of the blood, among then carbon dioxide. The Van Slyke apparatus, however, cannot be directly applied to the analysis of carbonates in general with facility.

A combination of the principles of Dr. Van Slyke and of the nitrometer has solved the difficulty and resulted in the development of the present apparatus.

APPARATUS

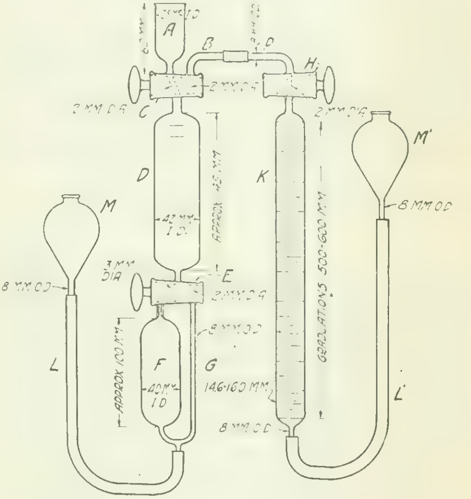
The apparatus consists of a reaction bulb, D, of about 200-cc. capacity, calibrated from the top downward to indicate 10-, 25-, 50-, and 100-cc. capacities. At the upper end it is connected with a 2-way stopcock, C, carefully ground so as to be vacuum-tight when greased. C connects with a cup, A, of approximately 25-cc. capacity, and with a large capillary tube, B, bent at right angles. The lower end of D is connected to a 2-way stopcock, E. This stopcock connects at one outlet with the tube G, and at the other with the bulb F, of about 125-cc. capacity. At the other end the bulb F joins the tube G, and through a hose connection is joined by means of rubber pressure tubing, L, to the mercury reservoir M, of about 500-cc. capacity. K is a gas measuring buret of ordinary type used in nitrometer work and is calibrated from 0 cc. to 100 cc. in 0.2-cc. intervals.

The stopcock and seats are carefully cleaned and greased, B and P connected with pressure tubing, the train filled with mercury and tested under vacuum for air leaks, giving special attention to C and E. The apparatus is now ready for the analysis.

ANALYSIS

The sample is introduced into D from A by means of stopcock C. It may be measured previously by a pipet or buret into A, or it may be measured by drawing into D to the desired calibration. The latter method is sometimes desirable when analyzing a sample containing free carbon dioxide in large amount. By means of a 2-hole rubber stopper with inlet and outlet tube fitted into the top of A, a portion of the liquid to be analyzed may be used to fill and flush out A, thus assuring no mechanical loss of carbon dioxide during the introduction of the sample. If free carbon dioxide alone is desired no acid is added at this point, but if total carbon dioxide is required concentrated sulfuric acid is added by means of cup A and stopcock C till in distinct excess. D is then agitated to mix the water and acid thoroughly, and any gas formed is passed over into K, allowing none of the liquid to pass out of D. The mercury level in K and M is adjusted, stopcock H is closed, and an approximate reading of the gas in K is taken, temporarily disregarding the gas in the capillary. The reservoir M is then lowered and the mercury is drawn from D through the tube G, tending to form a Torricelli vacuum in D. When most of the mercury has been drawn from D, the stopcock E is turned so as to deliver into bulb F. The rest of the mercury and the sample are completely drawn from D into F. E is then closed, imprisoning the sample in F. M is raised and E is turned so as to connect G with D. The mercury will then rise in D. The gas liberated by the evacuation may then be passed over into K and an approximate reading taken, noting the increase.

M is again lowered and most of the mercury drawn from D through G. When D has been nearly emptied, M is raised and E turned so as to permit the sample to pass from F to D. In doing so it is converted into a fine stream which is flattened against the sides of the glass and agitated by the mercury in such a manner that a large surface is exposed to the vacuum in D, thus aiding the liberation of dissolved gas. M is again lowered, the sample imprisoned in F and the mercury are allowed to flow back through G to D, and any gas is passed over into K, and the increase noted. The evacuations are continued till the increase has become negligible. Three to four evacuations are usually required. The gas in the capillary is then displaced with mercury and the gas volume in K read, with the usual precautions taken for such readings. The temperature and pressure are of course noted and corrections made accordingly. If the gas is not dry when the volume is read, correction for moisture must also be made.



A determination can be made with this apparatus in from 15 to 30 min., and a maximum of 3 per cent of error is indicated, though a higher degree of accuracy is usually obtained.

This method was checked in various ways. The exact amount of carbon dioxide present in a sodium bicarbonate solution of approximately 0.5 *N* strength was determined gravimetrically with barium hydroxide. This proved to be 10.142 g. of CO_2 per liter, which is equivalent to 5.14 cc. of CO_2 (at 0° C. and 760 mm.) per cc. of solution. In running the tests with this solution, varying amounts of sample were taken and varying concentrations of acid were used. Table I shows results obtained with this solution:

---

[1] Received July 26, 1921.

[2] *J. Am. Chem. Soc.*, **37** (1915), 2490.

[3] *J. Biol. Chem.*, **30** (1917), 347.

TABLE I

Cc. of Sample Taken	Conc. Sulfuric Acid Used Cc.	—CO₂ at 0° C. and 760 Mm.— in Sample Cc.	Found Cc.	Error Per cent
1.94	20	9.98	9.71	2.7
1.94	20	9.98	9.8	1.8
10	..	51.4	51.3	0.19
10	15	51.4	49.9	2.7
10	Slightly acidified	51.4	50.5	1.75

Certain of the above-measured gas volumes were passed into caustic and showed practically complete absorption. In addition, a 25-cc. portion of the bicarbonate solution was evacuated without acidifying. A reading of 1.7 cc. was obtained, equivalent to a blank of 0.068 cc. of gas per 1 cc. of sample or slightly less than 1.4 per cent of error. When, however, we consider that a part of this blank was undoubtedly due to a decomposition of the bicarbonate under very greatly reduced pressure the error approaches the vanishing point. In this connection, 25 cc. of ordinary distilled water were acidified and evacuated and a reading of less than 0.4 cc. found. This represents 0.3 per cent error, as compared with 1.4 per cent.

Another check was run upon the method by passing carbon dioxide through approximately 0.05 *N* sulfuric acid. This 0.05 *N* acid represented the approximate free mineral acidity of some of the mine water with which the author was working and was used as another standard solution.

The carbon dioxide was determined by the modified nitrometer method and by the titrimetric method (phenolphthalein cold—phenolphthalein hot) using 0.1 *N* sodium hydroxide. The sample was allowed to stand in the laboratory in a large, poorly stoppered bottle for 6 hrs., and again analyzed by both methods.

Table II shows the results obtained:

TABLE II

	Carbon Dioxide P. p. m.
10:00 A. M.	
Titration	402
Gasometric	422[1]
4:00 P. M.	
Titration	354
Gasometric	381[1]

[1] Caustic absorption practically complete.

Since the prevailing tendency of the gasometric method is, under these conditions, low, the above figures, while hardly conclusive, indicate that the growing opinion against phenolphthalein as an indicator in carbon dioxide titrations is well founded. Numerous other determinations were made which gave logical, consistent figures.

It is believed that the apparatus as outlined can be conveniently adapted to field work. It was not found necessary to assemble the apparatus for this purpose, but the matter has been given some consideration for possible future use. There appear to be no difficulties that cannot be readily overcome. Care will be taken to standardize properly the dimensions of the apparatus.

The Effect of the Presence of Filter Paper on Permanganate-Oxalate Titrations[1]

By Stephen G. Simpson

ANALYTICAL LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

In the analysis of limestone, lime, and cement, the determination of calcium is most rapidly made by titrating a hot acid solution of the precipitated calcium oxalate with permanganate. To insure complete solution of the oxalate from the filter paper, many analysts find it most convenient to add the paper itself to the solution and to allow it to remain suspended in the liquid during the titration. Indeed, the American Society for Testing Materials[2] has adopted such a procedure as a tentative method for analyzing limestone and lime although in the method as given, the greater part of the calcium oxalate is washed from the filter paper with hot water and the paper containing the remainder of the oxalate[3] is added to the solution near the end of the titration. Several textbooks give essentially the same procedure.[4] The fact that permanganate may be reduced by filter paper shreds is generally known, and Myhill[5] has recently emphasized this point in connection with permanganate titrations. For this reason, Gooch[6] filters the calcium oxalate upon asbestos, and others[7] dissolve from the filter paper by means of prolonged washing with hot, dilute sulfuric acid. The extent of this reduction under the conditions of ordinary volumetric titrations is not given, however, and whether or not the effect is great enough to affect appreciably the accuracy of ordinary analytical results is not generally known.

EXPERIMENTAL DETAILS

In the following experiments 0.1 *N* solutions of oxalic acid and potassium permanganate were used, and all titrations were made by means of weighing burets. The ratio of permanganate to oxalic acid was repeatedly established during each series of experiments, and in all determinations the end-point was taken as a faint pink remaining permanent for at least 15 sec. The filter papers were Baker and Adamson's 9-cm. washed papers weighing approximately 0.45 g. each. Since the extent of disintegration and hence the reducing power of the filter paper could not be accurately controlled, it could hardly be expected that the results obtained under apparently similar conditions would be in perfect agreement, but the values obtained checked closely enough to give a fairly accurate idea of the extent of reduction in each case.

The first and second series of titrations were carried out with the object of determining under varying conditions of time and concentration the extent of reduction of an excess of permanganate when kept in contact with filter paper. In the first series, 60 drops (4.6 cc.) of 0.1 *N* $KMnO_4$ were added from a weighing buret to 350 cc. of water containing 20 cc. of 6 *N* H_2SO_4 and heated to 70° C. A filter paper was submerged in the solution and allowed to remain for a

TABLE I—REDUCTION OF 0.1 *N* POTASSIUM PERMANGANATE BY FILTER PAPER, VARYING TIME OF CONTACT

Vol. $KMnO_4$ = 4.6 cc. Vol. soln. = 350 cc. Conc. $KMnO_4$ = 0.042 g./l.

Time of Contact Min.	Total Vol. $H_2C_2O_4$ Cc.	Total Vol. $KMnO_4$ Cc.	$KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 *N* $KMnO_4$ Reduced Cc.
1	4.38	4.71	4.57	0.14
1	4.59	4.95	4.79	0.16
1	4.40	4.76	4.60	0.16
3	4.23	4.67	4.42	0.25
3	4.37	4.79	4.56	0.23
3	4.57	5.02	4.77	0.25
7	4.20	4.72	4.38	0.34
7	4.10	4.62	4.28	0.34
7	4.18	4.73	4.37	0.36
20	4.06	4.75	4.24	0.51
20	4.20	4.86	4.38	0.48
20	4.48	5.19	4.68	0.51

[1] Ratio = 1.044.

---

[1] Received July 5, 1921.

[2] *Proc. Am. Soc. Testing Materials*, **20** (1920), 632.

[3] Hot water will not remove all the calcium oxalate from the paper. See U. S. Geological Survey, *Bulletin* **700**, 147.

[4] Low, "Technical Methods of Ore Analysis;" Cheever-Smith, "Select Methods in Quantitative Analysis."

[5] *Chem. Age* (*London*), **4** (1921), 151.

[6] Gooch, "Methods in Chemical Analysis."

[7] Sutton, "Volumetric Analysis;" Treadwell-Hall, "Analytical Chemistry," II.

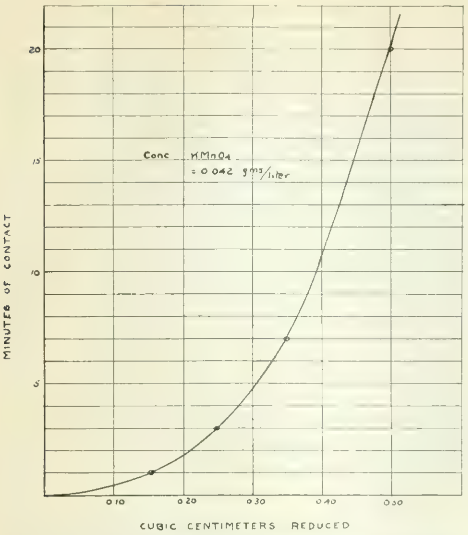


FIG. 1—GRAPH SHOWING REDUCTION OF POTASSIUM PERMANGANATE BY CONTACT WITH FILTER PAPER UNDER CONDITIONS GIVEN IN TABLE I. RESULTS IN TERMS OF 0 1 N KMnO₄

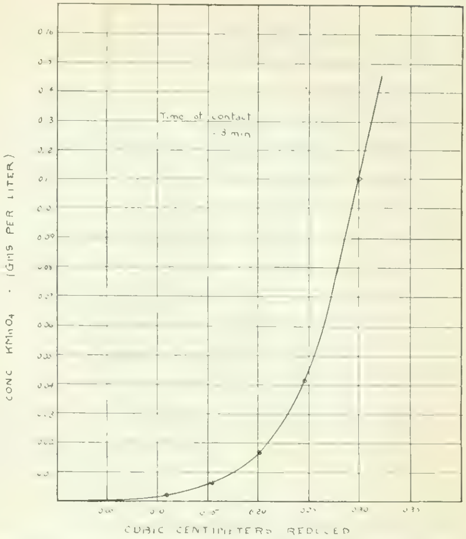


FIG. 2—GRAPH SHOWING REDUCTION OF POTASSIUM PERMANGANATE BY CONTACT WITH FILTER PAPER UNDER CONDITIONS GIVEN IN TABLE II. RESULTS IN TERMS OF 0.1 N KMnO₄

specified length of time, during which the solution was occasionally stirred and the paper allowed to disintegrate only of its own accord. An excess of the standard oxalic acid was quickly added and the titration was finished with the permanganate. The volume of permanganate used up by the filter paper was calculated in each case in terms of 0.1 N $KMnO_4$, and the values obtained are given in Table I. Similar titrations were made keeping the time of contact with the filter paper constant and varying the concentration of the excess permanganate. The numerical results of this series in terms of 0.1 N $KMnO_4$ are given in Table II. Figs. 1 and 2 show in graphic form the averages of the results given in Tables I and II. From these graphs it is seen that the reduction of permanganate by filter paper increases very rapidly with the first few drops of excess permanganate and in the first few moments of contact—facts which in themselves show the danger of titrating with permanganate in the presence of filter paper.

TABLE II—REDUCTION OF 0.1 N POTASSIUM PERMANGANATE BY FILTER PAPER, VARYING CONCENTRATION OF EXCESS PERMANGANATE

Time of Contact = 3 Min.

Vol $KMnO_4$ Cc.	Vol. Soln. Cc.	Conc. $KMnO_4$ G./L.	Total Vol. $H_2C_2O_4$ Cc.	Total Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 N $KMnO_4$ Reduced Cc.
0.24	350	0.0022	0.49	0.62	0.51	0.11
0.24	350	0.0022	0.20	0.32	0.21	0.11
0.24	350	0.0022	0.26	0.38	0.27	0.11
0.77	350	0.0070	0.92	1.11	0.96	0.15
0.77	350	0.0070	0.76	0.95	0.79	0.16
0.77	350	0.0070	0.77	0.96	0.81	0.15
1.9	350	0.017	1.75	2.03	1.83	0.20
1.9	350	0.017	1.72	2.02	1.80	0.22
1.9	350	0.017	2.20	2.48	2.29	0.19
4.6	350	0.042	4.23	4.67	4.42	0.25
4.6	350	0.042	4.37	4.79	4.56	0.23
4.6	350	0.042	4.57	5.02	4.77	0.25
4.6	125	0.110	4.26	4.74	4.44	0.30
4.6	125	0.110	5.24	5.78	5.47	0.31
4.6	125	0.110	4.19	4.67	4.38	0.29

[1] Ratio = 1.044.

In the third series of titrations, 200 cc. of water containing 20 cc. of 6 N H_2SO_4 were heated to 70° C., standard oxalic acid was added from a weighing buret, a filter paper was submerged in the liquid, and the solution was titrated with the standard permanganate. In each titration the permanganate was added slowly, allowing the solution to become decolorized between each drop, and the filter paper was broken up as little as possible. The results given in Table III show that, under the given conditions, the average volume of 0.1 N $KMnO_4$ reduced by the filter paper is about 0.03 cc.

TABLE III—REDUCTION OF 0.1 N POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATION

Vol. $H_2C_2O_4$ Cc.	Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 N $KMnO_4$ Reduced Cc.
2.674	2.786	2.758	0.028
2.082	2.176	2.148	0.028
2.569	2.674	2.651	0.023
2.566	2.689	2.647	0.042
2.674	2.790	2.759	0.031
1.979	2.078	2.043	0.035
3.211	3.338	3.313	0.025
4.024	4.176	4.152	0.024
			Av. 0.030

[1] Ratio = 1.032.

As in all permanganate-oxalate titrations, with the first few drops of permanganate the resulting solution is decolorized only very slowly, during which time the permanganate may be very appreciably reduced by any filter paper shreds present. This source of error may be reduced either by adding a few cubic centimeters of manganous sulfate solution previous to the titration, or by adding the filter paper shortly before the completion of the titration as mentioned above. The effect of the previous addition of manganous sulfate is shown in Table IV, and the effect of adding the filter paper late in the titration is shown in Table V where, incidentally,

TABLE IV—REDUCTION OF 0.1 N POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATIONS, ADDING MANGANOUS SULFATE

Vol. $H_2C_2O_4$ Cc.	Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 N $KMnO_4$ Reduced Cc.
2.057	2.132	2.122	0.010
3.131	3.249	3.229	0.020
3.628	3.754	3.744	0.010
3.306	3.432	3.411	0.021
3.478	3.605	3.588	0.017
5.225	5.414	5.392	0.022
			Av. 0.017

[1] Ratio = 1.032.

the total volume of $KMnO_4$ used is more nearly comparable to the volume used in an average limestone or cement analysis. In each case the average reduction of permanganate is decreased by about 50 per cent, or to a point where the error is hardly greater than the error involved in reading an ordinary buret.

TABLE V REDUCTION OF 0.1 *N* POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATIONS, ADDING FILTER PAPER WITHIN ABOUT 2 CC. OF THE END-POINT

Vol. $H_2C_2O_4$ Cc.	Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 *N* $KMnO_4$ Reduced Cc.
18.675	19.120	19.105	0.015
26.264	26.892	26.868	0.024
20.716	21.203	21.193	0.010
11.914	12.203	12.188	0.015
43.990	45.014	45.002	0.012
			Av. 0.015

[1] Ratio = 1.023.

Similar titrations in the presence of filter paper which had been thoroughly disintegrated gave such fugitive end-points, and were accompanied by such considerable reductions of permanganate, that it would be impossible under such conditions to obtain even approximately correct results.

SUMMARY

1—The reduction of potassium permanganate by filter paper increases rapidly with the first few drops of excess permanganate and in the first moments of contact.

2—In titrating oxalates with permanganate in the presence of filter paper, except in cases where great accuracy is required, satisfactory results may be obtained either by previously adding a small amount of manganous sulfate and titrating slowly, taking great care not to disintegrate the paper; or better by washing most of the oxalate from the paper with hot water and adding the paper only when the titration is nearly complete. In either case, the error caused by the presence of the filter paper is hardly greater than the error involved in the reading of an ordinary buret.

3—Satisfactory results cannot be obtained in any case where the filter paper is present in highly disintegrated form.

The Formation of Oxides of Nitrogen in the Slow Combustion and Explosion Methods in Gas Analyses[1,2,3]

By G. W. Jones and W. L. Parker

BUREAU OF MINES, PITTSBURGH, PENNSYLVANIA

INTRODUCTION

As a part of its investigation pertaining to a more efficient utilization of the natural resources of the country and greater safety in mining methods, the Bureau of Mines has occasion to make many analyses of gases from mines. These gases vary from samples of mine air taken under good ventilation conditions to those from mine fires and gases after explosion disasters and the like.

The accuracy of analysis is important, and constant endeavor is made to develop better methods and refinements in gas analysis.

This report deals with the production of oxides of nitrogen when gases are analyzed by the slow combustion and explosion methods under the usual conditions of analysis.

PURPOSE OF INVESTIGATION

The question relative to the production of oxides of nitrogen when combustible gases are burned by slow combustion using a glowing platinum spiral, or by explosion using an electric spark, has been much discussed by authorities on gas analyses.

White[4] finds that large errors result when combustible gases are burned by the slow combustion method and attributes these errors to oxides of nitrogen, since tests made with Greiss's reagent give positive results, and concludes that the slow combustion method is unreliable for accurate gas analysis. Dennis,[5] on the other hand, finds that, "when the spiral was heated for 5 min. to a temperature of dull redness in 100 cc. of air, the colorimetric determination of the nitrite that was formed showed that the amount of the oxides of nitrogen produced did not in any case exceed 0.005 cc. and that the volume is usually much less than this." Dennis further states that under the most unusual conditions the volume of oxides of nitrogen formed was less than 0.01 cc., which in technical gas analysis is inappreciable.

The greater part of the routine analytical work in gas analysis at the Pittsburgh Experiment Station of the U. S. Bureau of Mines consists in the analysis of samples of gases from metal and coal mines. The percentages of total combustibles in these samples are very low, in most cases less than 0.2 of one per cent. For this work gas apparatus of the Haldane type as modified by Burrell[1] is used.

Haldane apparatus is so constructed that volumes can be read to an accuracy of about 0.002 cc. It has a limit of accuracy of about 0.02 per cent when the three combustible gases, methane, carbon monoxide, and hydrogen, are present.

In this method the combustibles are burned with a platinum spiral heated to a bright yellow. It is evident that if appreciable amounts of oxides of nitrogen are formed this method cannot be used since contractions would be produced even when combustibles were absent. When normal air is passed into the slow combustion pipet and the spiral heated to a bright yellow for 3 min., the contraction produced seldom exceeds 0.005 cc. and in most cases is found to be less than 0.002 cc.

To prove or disprove whether these small contractions were due to oxides of nitrogen, ten different platinum wires of No. 28 B & S gage were investigated under conditions as used in analysis.

The wires, 2.25 in. long and wound into a spiral as used in gas analysis, were heated for different periods of time, and at different temperatures, and the resulting gases analyzed for oxides of nitrogen by the method to be described. The greater number of the tests were made with normal air containing no combustible since this condition more nearly approximates the condition in actual use.

OXIDES OF NITROGEN BY THE SLOW COMBUSTION METHOD

The procedure of making the tests was essentially as follows: The platinum wire to be tested having been assembled in the combustion pipet of the Haldane apparatus, about 20 cc. of laboratory air were drawn into the buret and accurately measured, then passed into the KOH pipet and the carbon dioxide removed. The gas volume was again read, passed into the combustion pipet, and burned for a determined

---

[1] Received August 3, 1921.

[2] Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[3] Published by permission of Director, U. S. Bureau of Mines.

[4] "The Oxidation of Nitrogen as a Source of Error in the Estimation of Hydrogen and Methane," *J. Am. Chem. Soc.*, **23** (1901), 476.

[5] "Gas Analysis," **1913**, 152.

[1] G. A. Burrell and F. M. Seibert, U. S. Bureau of Mines, *Bulletin* **42**, "The Sampling and Analyses of Mine Gases and Natural Gas."

length of time, at a temperature designated as dull red, bright red, and bright yellow. After the gas was cooled to room temperature it was withdrawn into the buret and the contraction read. The gas was then passed slowly from the buret through a Bowen's absorption tube containing 5 cc. of 10 per cent sodium hydroxide solution. The sodium hydroxide solution absorbed the oxides of nitrogen which were assumed to be in the form of nitric oxide (NO) and nitrogen peroxide ($NO_2 + N_2O_4$). This solution was tested quantitatively for oxides of nitrogen by the following method.

DETERMINATION OF OXIDES OF NITROGEN

The method used to determine the oxides of nitrogen was developed from the usual procedure for the determination of these constituents in water analysis,[1] using the diphenylsulfonic acid method. Nitric oxide in the presence of oxygen is almost completely oxidized to nitrogen peroxide, which in turn forms nitrous and nitric acid in the presence of water vapor. Nitric oxide is also completely oxidized to the peroxide[2] when treated with hydrogen peroxide and sodium hydroxide and boiled on a hot plate. A solution of potassium permanganate may be used in place of hydrogen peroxide for oxidizing the nitrites to nitrates. Care must be taken not to add an excess, otherwise the potassium permanganate interferes in matching the color standards. The nitrates formed are subsequently determined by the usual procedure of water analysis.

REAGENTS—*Phenolsulfonic Acid*—Twenty-five grams of pure white phenol are dissolved in 150 cc. of concentrated sulfuric acid, 75 cc. of fuming sulfuric acid (15 per cent SO_3) are added, stirred, and the mixture is heated for 2 hrs. at 100° C.

Standard Nitrate Solution—A solution is made containing 0.72 g. of potassium nitrate per liter. Ten cc. of this solution are evaporated on a water bath until about one drop is left and the remaining water removed with a current of dry air. The residue is thoroughly moistened with 2 cc. of the phenoldisulfonic acid solution and made up to 1 liter. One cc. of this solution equals 0.001 mg. of nitrogen.

Sodium Hydroxide—A 10 per cent solution of chemically pure sodium hydroxide is used.

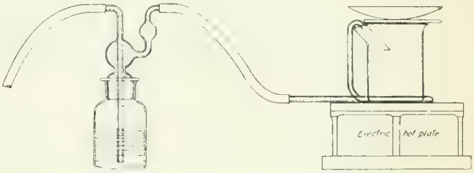
Ammonium Hydroxide Solution—Equal parts of concentrated ammonium hydroxide and distilled water are used.

PREPARATION OF STANDARDS—A set of standards was made by measuring the required amounts of the standard potassium nitrate into Nessler tubes, adding 5 cc. of ammonium hydroxide solution and diluting each to 100 cc. with distilled water.

The standards had the following values:

Standard No.	Standard KNO_3 Solution Cc.	Value of Standard Cc. NO_2 at 0° C. and 760 Mm. Hg
1	0	0.0000
2	1	0.0018
3	2	0.0035
4	4	0.0070
5	7	0.0133
6	10	0.0176
7	15	0.0263
8	20	0.0355
9	25	0.0438
10	30	0.0525
11	35	0.0613
12	40	0.0700

PROCEDURE—After the oxides of nitrogen were taken up by the sodium hydroxide solution, this solution was transferred to an evaporating dish, 5 cc. of hydrogen peroxide were added, and it was allowed to stand 30 min. The solution was evaporated almost to dryness on a hot plate, then completely on a water bath. The evaporation was hastened by an arrangement shown in the figure, whereby heated dry air was blown over the surface of the liquid. A glass tube lying on the hot plate encircled the beaker, then rose and projected down over the rim of the beaker for about 1 in. A gentle stream of dry air free from oxides of nitrogen was passed through the tube, keeping a small excess pressure on the inside of the beaker and so prevented contamination from the room air. The last final evaporation was finished on a water bath. When dry the residue was moistened with 2 cc. of the phenoldisulfonic acid, diluted with 10 cc. of distilled water, and run through a filter paper into a Nessler tube. After the usual rinsing and washing, 15 cc. of the ammonia solution were added and the whole made up to 100 cc. and compared with the standards. A blank was run at the same time with the sample.



In case the color was too intense to come within the range of the color standards, the sample was diluted with distilled water until the color was diminished sufficiently to make comparisons and the correct value calculated from the amount of dilution.

RESULTS OF TESTS

Table I gives the results obtained by testing different platinum wires. Nos. 1 to 7, inclusive, were ordinary grades of platinum wire sold for combustion purposes. No. 8 con-

TABLE I—CC. OF OXIDES OF NITROGEN PRODUCED BY DIFFERENT PLATINUM WIRES WHEN HEATED FOR DIFFERENT LENGTHS OF TIME AND DIFFERENT TEMPERATURES
(Oxides of nitrogen reported as NO_2—20 cc. of gas used in each test)

TEST No.	Time of Burning, Min.	Temp. of Wire[1]	Contraction of Gas Due to Burning, Cc.	Blank NO_2 of Solutions, Cc.	NO_2 Found, Cc.	NO_2 Produced, Cc.	REMARKS
1-A-3	3	A	0.008	0.004	0.007	0.003	Laboratory air
1-A-2	2	A	0.005	0.004	0.005	0.001	Laboratory air
1-A-1	1	A	0.000	0.004	0.005	0.001	Laboratory air
1-B-3	3	B	0.000	0.004	0.004	0.000	Laboratory air
1-B-2	2	B	0.004	0.004	0.004	0.000	Laboratory air
1-B-1	1	B	0.001	0.004	0.004	0.000	Laboratory air
1-C-3	3	C	0.000	0.004	0.004	0.000	Laboratory air
1-C-2	2	C	0.000	0.004	0.004	0.000	Laboratory air
1-C-1	1	C	0.002	0.004	0.004	0.000	Laboratory air
2-A-3	3	A	0.003	0.004	0.004	0.000	Laboratory air
2-A-2	2	A	0.002	0.004	0.004	0.000	Laboratory air
2-B-3	3	B	0.000	0.004	0.004	0.000	Laboratory air
2-C-3	3	C	0.000	0.004	0.004	0.000	Laboratory air
3-A-3	3	A	0.009	0.004	0.004	0.000	Laboratory air
3-A-2	2	A	0.003	0.004	0.004	0.000	Laboratory air
3-B-3	3	B	0.004	0.004	0.004	0.000	Laboratory air
3-B-2	2	B	0.000	0.004	0.004	0.000	Laboratory air
3-C-3	3	C	0.000	0.004	0.004	0.000	Laboratory air
4-A-3	3	A	0.000	0.004	0.004	0.000	Laboratory air
4-B-3	3	B	0.000	0.004	0.004	0.000	Laboratory air
5-A-3	3	A	0.006	0.002	0.003	0.001	Laboratory air
5-A 1	1	A	.....	0.002	0.002	0.000	2 per cent CH_4 and air mixture
5-B-3	3	B	0.005	0.002	0.002	0.000	Laboratory air
6-A-3	3	A	0.003	0.002	0.004	0.002	Laboratory air
6-B-3	3	B	0.008	0.002	0.001	0.001	Laboratory air
7-A-3	3	A	0.002	0.002	0.002	0.000	Laboratory air
7-A-12	12	A	0.007	0.002	0.005	0.003	Laboratory air
8-A-3	3	A	0.002	0.005	0.006	0.001	Laboratory air
8-B-3	3	B	.....	0.005	0.006	0.001	Laboratory air
8-C-2	2	C	0.000	0.005	0.005	0.000	Laboratory air
8-A-2	2	A	.....	0.005	0.006	0.001	2 per cent CH_4 and air mixture
9-A-3	3	A	0.004	0.005	0.006	0.001	Laboratory air
9-A-2	2	A	.....	0.005	0.005	0.000	Laboratory air
9-B-3	3	B	0.000	0.003	0.006	0.001	Laboratory air
9-B-1	1	B	0.000	0.005	0.005	0.000	Laboratory air
9-B-2	2	B	.....	0.005	0.006	0.001	2 per cent CH_4 and air mixture
10-A-2	2	A	0.004	0.005	0.005	0.000	Laboratory air
10-B-3	3	B	0.000	0.005	0.005	0.000	Laboratory air

[1] A = bright yellow; B = bright red; C = dull red.

---

[1] "Standard Methods of Water Analysis," American Public Health Association, **1917**, 3rd Ed., 23.

[2] R. R. Tatlock and R. T. Thompson, "The Analysis of Waters and Their Changes in Composition When Employed in Steam Raising," *J. Soc. Chem Ind.*, **23** (1914), 428.

tained a small amount (less than 5 per cent) of iridium. No. 9 was platinum gauze, containing 10 per cent palladium gauze. No. 10 was pure palladium gauze.

Each wire was tested at the different temperatures and the different lengths of time given in the table. The contractions produced on burning the total oxides of nitrogen and the net oxides of nitrogen after subtracting the blank are given.

From the table it is seen that the maximum quantity of oxides of nitrogen produced was only 0.003 cc., a value within the experimental error for routine gas analysis. This quantity was produced by using a bright yellow heat and burning for 3 min.

In the greater majority of tests, the oxides of nitrogen were found to be zero.

That little if any oxides of nitrogen should be produced by the slow combustion method is indicated by values given by Nernst.[1]

Nernst found the following values when equilibrium between $N_2 + O_2 \rightleftarrows 2NO$ was established.

TEMPERATURE ° C.	Volume NO Observed Per cent
1500	0.10
1538	0.37
1604	0.42
1760	0.64
1922	0.97
2000	1.20
2500	2.60
3000	5.30

The time required to form one-half the concentration of NO at equilibrium conditions from air is given by Jellinek[2] as follows:

Absolute Temperature ° C.	Time of Formation of Half the Possible Concentration of NO from Air
1000	81.62 yrs.
1500	1.26 days
1900	2.08 min.
2100	5.06 sec.

Taking 1500° C., the highest temperature at which the platinum wire is used (platinum melts at 1733°), it would require a longer time than 3 min. (the maximum time a wire is used in most gas analysis) to produce one-half the concentration as given above, providing there is no catalytic effect due to the platinum wire. Since, according to the values given by Nernst, only 0.10 per cent NO is produced at 1500° C., the amount of oxides of nitrogen at 1500° C. would not be over 0.05 per cent with burnings of 3-min. duration.

To supplement the values obtained in Table I where mostly laboratory air was used in the tests, three tests were made on an Orsat apparatus with larger amounts of combustibles. The presence of combustibles were suggested as being favorable for the production of oxides of nitrogen.

The results are given below:

Test No.	Gas	Gas Cc.	Air Cc.	O_2 Cc.	Blank NO_2	Total NO_2	NO_2 Obtained Cc.
1	H_2	5.5	92.5	0.0	0.005	0.005	0.000
2	H_2	12.6	85.2	0.0	0.005	0.005	0.000
3	CH_4	20.1	41.5	41.5	0.005	0.005	0.000

Wire heated to a bright yellow.

This table shows that no oxides of nitrogen are produced when combustibles are burned in air, or mixtures of oxygen and air, when the wire is heated to a bright yellow, the usual temperature used in slow combustion methods.

OXIDES OF NITROGEN BY THE EXPLOSION METHOD

A series of tests were made for oxides of nitrogen by exploding synthetic gas mixtures in a Morehead buret and examining the residual gases for oxides of nitrogen as previously described. Since water is used in the Morehead buret it was necessary to use distilled water for each test and to change the analytical procedure somewhat.

TABLE II—RESULTS OF TESTS OF OXIDES OF NITROGEN PRODUCED BY THE EXPLOSION METHOD

Test No.	—Gases Used for Explosion, Cc.— H_2	CH_4	Air	Oxygen	NO_2 Found Cc.	Blank NO_2 Cc.	Net NO_2 Cc.
1	5.5		92.5	....	0.005	0.005	0.000
2	12.6	....	85.2	....	0.005	0.005	0.000
3	15.2	....	84.2	....	0.005	0.005	0.000
4	25.2	....	75.2	....	0.005	0.005	0.000
5	30.0	....	70.2	....	0.005	0.005	0.000
6	50.2	....	49.3	....	0.005	0.005	0.000
7	59.8	....	39.8	....	0.005	0.005	0.000
8[1]	69.5	....	30.3	...	.....	.....	.....
9	30.0	....	49.6	5.2	0.011	0.005	0.006
10	39.7	....	46.0	14.6	0.050	0.005	0.045
11	49.7	....	26.2	24.9	0.163	0.005	0.158
12	....	8.2	92.0	....	0.005	0.005	0.000
13	....	9.8	89.7	....	0.005	0.005	0.000
14	....	12.2	87.7	....	0.005	0.005	0.000
15	....	14.2	85.8	....	0.005	0.005	0.000
16	....	10.5	80.0	7.5	0.011	0.006	0.005
17	....	10.4	67.9	21.6	0.125	0.005	0.120
18	....	15.0	39.8	25.0	0.150	0.006	0.144
19	....	15.0	50.8	25.2	0.163	0.006	0.157
20	....	14.0	66.0	20.0	0.285	0.005	0.280
21	....	12.9	66.5	20.6	0.350	0.005	0.345
22	16.5	4.7	5.1	23.0	0.200	0.005	0.195

[1] Did not explode.

The different gas mixtures given in Table II were introduced into the buret and measured. After the gases were thoroughly mixed, a spark was passed across the electric terminals and the gases exploded. After the explosion sodium hydroxide solution was added to the buret in small amounts at a time and allowed to stand 1 hr. or more to insure complete absorption of the oxides of nitrogen. All the water and hydroxide solution mixed with the water was then withdrawn and used for the test for oxides of nitrogen.

DISCUSSION OF TABLE II

The results of the tests are given in Table II. The volume of oxides of nitrogen varied from 0 to 0.345 cc. When air was used for the oxygen supply, no oxides of nitrogen were produced when either hydrogen or methane was exploded. The proportions of air to gas were varied from the lower to the upper explosive limit for both hydrogen and methane.

When a mixture of oxygen and air was used for the explosion, varying amounts of oxides of nitrogen were formed depending upon the proportions used.

These tests indicate that oxides of nitrogen are not produced in detectable quantities by the sparks between the terminals, but are rather a result of the flame temperature produced when the gases are exploded. The flame temperature of gas-air mixtures is lower than gas-oxygen mixture, due to the inert nitrogen present in air. In other words, there exists a critical point of flame temperature above which oxides of nitrogen are formed.

That gases should not be analyzed with oxygen by the explosion method is apparent by inspection of Table II. In Test 20, 14 cc. of methane, 66 cc. of air, and 20 cc. of oxygen were used for the explosion, and 0.28 cc. of oxides of nitrogen was produced. This 0.28 cc. produces an error in the results of $\frac{0.28}{14}$, which equals 2 per cent in the final result. This error in the usual gas analysis, where analysis is made for methane and hydrogen, distributes itself between the two values. Some of the oxides of nitrogen produced are partly absorbed by the water before the contraction is read and the rest by the caustic potash.

CONCLUSIONS

1—The production of oxides of nitrogen by the slow combustion method when the time of burning is not more than 3 min. and the wire is not heated beyond a bright yellow is within the experimental error in routine gas analysis. Under the above conditions not more than 0.003 cc. of oxides of nitrogen is produced. The purity of the platinum wire has no effect on the quantity of oxides of nitrogen produced.

2—No oxides of nitrogen were produced by the explosion method when air was used as the oxygen supply.

---

[1] *Z. anorg. Chem.*, **49** (1906), 213; *Z. Elecktrochem.*, **12** (1906), 527.

[2] *Z. anorg. Chem.*, **49** (1906), 229.

3—When mixtures of air and oxygen were used as the oxygen supply in the explosion methods, appreciable quantities of oxides of nitrogen were formed which are too large to be disregarded in gas analysis. On a basis of 0.15 cc. of combustibles taken for analysis, the error due to oxides of nitrogen may vary 2 per cent in the calculated results when oxygen-air mixtures are used.

4—The production of oxides of nitrogen by the explosion method is due to the flame temperature developed by the gas mixture when exploded rather than to the sparking across the electrodes.

5—The addition of oxygen raises the flame temperature and reaches a critical point above which oxides of nitrogen are produced in appreciable quantities.

6—The method used for determining the quantity of oxides of nitrogen produced was accurate to 0.001 cc. and was a modification of the diphenolsulfonic acid method used in water analysis for determining oxides of nitrogen.

LABORATORY AND PLANT

Revised Specific Gravity Table for Orthophosphoric Acid at 25°/25° C.[1]

By **N. P. Knowlton** and **H. C. Mounce**

Laboratories of the Mallinckrodt Chemical Works, St. Louis, Missouri

In the course of routine analyses in this laboratory, it was very constantly observed that the relation between the strength and specific gravity of orthophosphoric acid, as determined, did not agree with published tables.

All the data available on the strength-specific gravity relation were examined and the figures found in the following sources were plotted for comparison: the 15° and 25° C. tables of the United States Pharmacopeia VIII, a table at 17.5° C. in Hager's Commentary on the German Pharmacopeia, a table at 15.5° C. by J. Watts,[2] and a table by Schiff.[3] When completed, this chart showed some very striking inconsistencies. For instance, the lines representing the tables of the U. S. P. VIII at 15° and 25° C. gave higher specific gravities for a given strength of acid than the tables of Hager, Schiff, and Watts, making due allowance for temperature differences. It was also found that the plotted lines were not uniform, and that the various curves were not parallel, the variations between the tables being much greater at some points than at others. This evident lack of accord in these tables prompted the present attempt to establish more accurately the true relationship between the specific gravity and strength of so important a substance.

Experimental

Orthophosphoric acid of about 90 per cent was purified by two recrystallizations. The various strengths were made by dilution of the crystallized acid with distilled water. Over 100 determinations of various strengths and specific gravities were made, at intervals of about 5 per cent, from 3.39 per cent up to 90.26 per cent. The specific gravity determinations were made in a 50-cc. pycnometer of the Reischauer type, with a neck of about 4-mm. bore. The temperature adjustments were made in a thermostat at 25° C. with a maximum variation of ±0.05° C. All figures represent apparent specific gravities, weighings having been made in air with brass weights. The strength determinations were made by the standard magnesium pyrophosphate gravimetric method. In order to check the accuracy of the method and manipulation, C. P. disodium orthophosphate, after several recrystallizations, was made anhydrous and assayed, using the same procedure as with the phosphoric acid itself. Two independent assays gave 100.05 and 99.97 per cent, respectively. A number of the solutions assayed were submitted to other workers, who independently checked the authors' results.

Table I is a compilation of the results obtained, each in close duplicate, with a maximum error of 0.05 per cent. There are also included the interpolated figures for specific gravity for the same percentages from the tables of the U. S. P. VIII, Watts, and Hager.

Table I

Per cent H_3PO_4 Determined	Apparent Sp. Gr. at 25/25° C. Determined	Apparent Sp. Gr. at 25/25° C. U.S.P. VIII	Apparent Sp. Gr. at 15/15° C. U.S.P. VIII	Sp. Gr. 15.5/15.5° C. J. Watts	Sp. Gr. 17.5/17.5° C. Hager
3.39	1.0187	1.019	1.019	1.018	1.016
5.66	1.0309	1.032	1.032	1.030	1.030
11.23	1.0616	1.064	1.065	1.062	1.063
11.44	1.0637	1.066	1.066	1.063	1.065
17.63	1.1009	1.104	1.105	1.100	1.102
21.55	1.1261	1.129	1.130	1.124	1.128
28.43	1.1715	1.176	1.178	1.170	1.175
31.17	1.1918	1.195	1.197	1.190	1.195
36.53	1.2289	1.235	1.238	1.228	1.233
48.12	1.3189	1.328	1.332	1.315	1.323
51.61	1.3506	1.359	1.362	1.347	1.354
53.23	1.3658	1.374	1.377	1.362	1.367
56.24	1.3911	1.401	1.405	1.391	1.394
61.91	1.4485	1.456	1.460	1.448	1.449
68.62	1.5131	1.524	1.528	....	1.518
74.45	1.5734	1.586	1.591	...	1.582
78.72	1.6195	1.634	1.638	...	1.631
78.87	1.6213	1.636	1.640	..	1.633
82.82	1.6659	1.681	1.684	....	1.679
83.62	1.6727	1.690	1.694	.....	1.688
85.62	1.7016	.....	...	.....	1.712
87.29	1.7188	...	..	.....	1.731
89.56	1.7479	....	..	.....	1.758
90.26	1.7558	....	....	.....	1.766

A computation of all the possible errors entering into these determinations indicates that the apparent specific gravities expressed in Column 2 are correct to within 0.0002 for the lighter acids, while the error for the higher gravities is slightly higher, owing to the difficulty in adjusting the meniscus in a viscous liquid.

This table shows very strikingly that the U. S. P. VIII figures for specific gravity are much higher than those of the other authorities. It will be noted also that Watts' results approximate very closely the authors' figures, when allowance is made for the difference in temperature.

Hager's table agrees rather closely with the authors' at a few points, but varies quite widely at others. The graphs representing these tables, if extended to 100 per cent, practically converge at a specific gravity of 1.8840. It is interesting to note that when actual determinations are reported in the literature the figures do not differ greatly from the authors' results, but that the completed tables show the greatest variations. From this it would seem that the tables have been compiled from a limited number of actual determinations, and that many of the figures represent interpolations or extrapolations.

The graph of our figures forms a perfectly smooth line of very slight, continuous curvature nearly analogous to the plotted line of Watts' table, whereas the curves of the U. S. P. VIII and Hager tables are represented by a number of broken straight lines.

From the plotted curve of our values for the determined

---

[1] Received August 8, 1921.

[2] *Chem. News*, **12** (1865), 160.

[3] *Ann.*, **113** (1860), 191.

apparent specific gravity at 25°/25° C. and strength of acid, Table II has been prepared.

TABLE II

Per cent H_3PO_4	Sp. Gr. at 25/25° C.	Per cent H_3PO_4	Sp. Gr. at 25/25° C.	Per cent H_3PO_4	Sp. Gr at 25/25° C.
1	1.005	32	1.197	62	1.449
2	1.011	33	1.205	63	1.457
3	1.016	34	1.212	64	1.467
4	1.022	35	1.219	65	1.477
5	1.027	36	1.226	66	1.486
6	1.033	37	1.233	67	1.496
7	1.038	38	1.241	68	1.506
8	1.044	39	1.249	69	1.516
9	1.049	40	1.256	70	1.527
10	1.055	41	1.264	71	1.537
11	1.060	42	1.271	72	1.547
12	1.066	43	1.279	73	1.558
13	1.073	44	1.286	74	1.569
14	1.079	45	1.294	75	1.579
15	1.085	46	1.302	76	1.589
16	1.091	47	1.310	77	1.600
17	1.097	48	1.318	78	1.611
18	1.103	49	1.327	79	1.622
19	1.110	50	1.336	80	1.633
20	1.116	51	1.345	81	1.644
21	1.123	52	1.354	82	1.655
22	1.129	53	1.363	83	1.667
23	1.135	54	1.372	84	1.678
24	1.142	55	1.381	85	1.690
25	1.149	56	1.390	86	1.702
26	1.155	57	1.399	87	1.715
27	1.162	58	1.409	88	1.728
28	1.169	59	1.419	89	1.740
29	1.176	60	1.429	90	1.753
30	1.183	61	1.439	91	1.766
31	1.190	..	.....	..	.....

A critical examination of all factors entering into this work indicates that, from Table II, the strength of mixtures of pure orthophosphoric acid and water can be calculated to an accuracy of about 0.05 per cent.

Graded Seal for Joining Pyrex to Lead Glass[1]

By **W. C. Taylor and Austin Bailey**

APPARATUS DIVISION, CORNING GLASS WORKS, CORNING, NEW YORK

In connection with research problems it is often necessary to join together apparatus whose parts are made of different kinds of glass, such as Pyrex, lime, and lead. Since these glasses have entirely different physical constants it is necessary to employ certain intermediate glasses with properties not so widely separated from one another. However, it is desirable to limit the number of glasses used in order to shorten the length of the seal and to decrease the labor required in its production.

Several patents[2] have been granted on methods of sealing quartz to glasses for the purpose of making vacuum-tight seals to leading-in wires.

Commercial graded seals from Pyrex to lead glass have so far been unsuccessful for several reasons. Intermediate glasses formed by mixing definite proportions of these two glasses all contained lead which caused blackening in the flame. Several of these intermediate glasses were subject to very rapid devitrification in heating and were commercially difficult to produce because of this same tendency. The number of such intermediate glasses required for a good seal was at least seven.

The authors have succeeded in developing a seal consisting of five glasses intermediate between Pyrex and lead glass. The glasses are all comparatively stable and can be worked repeatedly without devitrification. All of the intermediate glasses are of a lead-free borosilicate composition which makes the seal suitable to be worked in any ordinary blast lamp.

Of the factors which enter into the production of a satisfactory graded seal, the most important are expansion coefficient, viscosity, and softening point. The softening point is defined as that temperature at which a rod 1 mm. in diameter and 23 cm. long, the upper portion of which is heated in a furnace 15 cm. long, increases in length at the rate of 1 mm. per minute under its own weight. In making this seal the range of the softening point varies from 817° to 623° C. and the linear expansion coefficient varies from 0.0000032 to 0.0000089 per °C. The smallest differences in expansion coefficient lie between the intermediate glasses and the Pyrex and lead glass, respectively. This smaller difference is necessitated by a large difference in softening point at one end, and a large difference in composition and viscosity at the other.

In making up the graded seal the worker begins at the low expansion (Pyrex) end and after heating up the two consecutive glasses to such a temperature that the viscosities become approximately the same he blows the joint into its finished form. In cooling he partly reheats the lower expansion glass so that on final cooling it will pass through a greater range in temperature and thus approach more nearly the size of its nearest neighbor. He repeats the same operation over and over until the lead glass is finally sealed into place and the graded seal is complete.

---

[1] Received July 8, 1921.

[2] U. S. Patents 1,173,688 (February 29, 1916), to Elihu Thomson; 1,014,757 (June 16, 1912), to Keyes and Kraus; 1,191,630 (July 18, 1916), to Weintraub; Brit. Patent 18,300 (November 10, 1913), to British Thomson-Houston Co.

Plan Campaign for Standardization of Biological Stains

A meeting of representatives of scientific organizations, members of the National Research Council and others interested in obtaining and supplying biological stains of standard quality, was held at the Chemists' Club, New York, November 5, 1921. The meeting had been called by Dr. L. R. Jones, chairman of the Division of Biology and Agriculture of the National Research Council, and was presided over by him. The general need for standardized dyes or stains used in preparing and studying specimens in biological laboratories was discussed. It was the consensus of opinion that the standardization would have to be chemical as well as biological. It is a well-known fact that certain samples of methylene blue, for example, give a satisfactorily stained specimen, whereas other samples sold as methylene blue are totally unsatisfactory. The difference may be in the chemical analysis and in the reaction toward certain tissues.

Having agreed upon the general need for standardization, the Conference next turned to the selection of the proper organization or individuals to carry on such standardization. It was suggested that the coöperation of the various Government Bureaus and the National Research Council might be enlisted and their aid, together with the work of the scientists representing individual associations, would soon solve the problem. Representatives of the laboratories of the Department of Agriculture who were present volunteered their services, and the representative of the National Research Council stated that funds would be available for such clerical work as might be required.

In order to begin on a definite program, the Conference finally decided to work on the standardization of methylene blue, eosin, and gentian violet. Chemical analyses of available samples of these dyes will be made, and they will be tested out for efficiency as biological stains by representative zoölogists, bacteriologists, botanists, and scientists in the Color Laboratory of the Department of Agriculture. It is hoped that sufficient progress will have been made by the time of the meeting of the American Association for the Advancement of Science in December, so that standardized samples of these three dyes will be available for distribution and checking by laboratory men throughout the country. The Conference was composed of the following men: Dr. L. R. Jones, chairman, representing the National Research Council; Dr. McClung, representing the zoölogists; Dr. Conn, representing the bacteriologists; Dr. Hazen, representing the botanists; Drs. Ambler and Ball, representing the Department of Agriculture; Mr. H. E. Howe, representing the National Research Council; Mr. R. T. Will, representing the dealers in biological stains; and Mr. Keohan, representing the Chemical Foundation.

The Grasselli Medal of the Society of Chemical Industry is not to be awarded for 1921.

SPECIAL COST FACTORS AND THEIR RELATION TO THE DEVELOPMENT OF OUR ORGANIC CHEMICAL INDUSTRY[1]

By Gaston Du Bois

Monsanto Chemical Works, St. Louis, Missouri

We claim, and rightly so, that the quality of our American dyes is equal to that of German-made dyes, but unfortunately we cannot claim that our costs of production are no higher than the costs of production in Germany. In consequence of these abnormally high costs, we are losing the foreign markets to which we had begun to export our dyestuffs in gradually increasing quantities, as is shown in the 1920 Census of Dyes. From 1917 to 1920 we exported the following amount of dyes, expressed in dollars:

1917	$ 7,548,963.00
1918	15,266,520.00
1919	15,728,499.00
1920	29,823,591.00

However, during the first four months of 1921 our exports showed a marked decline:

January	$1,292,709.00
February	469,764.00
March	670,281.00
April	365,010.00

More than half of our exports in 1920 went to Asia and South America, but owing to our inability to meet foreign quotations, Germany is now rapidly reconquering these markets.

If we consider that in 1920, 23 per cent of our total production of dyes were exported, we can readily understand that the loss of foreign markets added to the present industrial depression must greatly affect our industry, and even should a majority in Congress understand our situation and decide to enact the necessary legislation to permit the American industry to supply the home demand for dyes, we should bear in mind that we cannot expect to export dyestuffs until we can produce at a competitive cost with Germany. If we are not able to do so, our volume of production must necessarily remain small as compared with the German production, and we shall be compelled to play second fiddle to the German combination.

In 1920 we produced 88,263,776 pounds of dyes, of which roughly 23 per cent were exported; therefore the home consumption amounted to 65 or 70 million pounds, which exceeds the imports of 1914 by 15 to 20 million pounds. The pre-war German production of dyes was in excess of 200,000,000 pounds, that is, more than three times the amount consumed in the United States in 1920, and more than four times the amount imported into the United States in 1914.

We can hope to be a factor in the world dye market only if we are able to produce the most important dyes at a competitive cost with Germany. At the present time our costs of production are two to three times higher than in Germany. If a certain dye is produced in Germany at a cost of 50 cents per pound, this same dye will cost here from $1.00 to $1.50 to produce and in some cases our cost will even exceed this ratio.

Some of the factors contributing to our high costs are well understood, and may simply be referred to here as:

1—Wages and salaries, which are to-day about seven times higher in the United States than in Germany.
2—Volume of production, which is inferior in the United States to that in Germany.
3—Yields and experience, which we can concede are generally superior in German plants producing dyes for thirty to forty years.

Five Important Factors

There are, however, some other important factors influencing costs which are not generally fully recognized, and the importance of which is frequently not fully appreciated even by a great majority of dye chemists and others responsible for the development of our dye industry, and it is to these special features which affect our costs that I wish to call your attention. These items, which are often included in "overheads," are:

Depreciation
Obsolescence
Idle plant cost
Insurance
Taxes

A study of these various items of cost leads us to the realization that, even though the war is over, its effect is still felt in these five items of cost fully as heavily as at any time since 1917.

Raw material prices, labor, coal, and other items of cost have dropped during the past year, but the high costs at which our dye plants were built during the war are bound to reflect on present costs of manufacture, owing to these five items.

How little consideration is given to these points by the average chemist can best be seen by the manner in which he will estimate the cost of manufacture of some intermediate or dye. We frequently hear the wildest statements made, in all good faith, regarding cost figures. There is an element of danger to our industry in such ill-advised statements, inasmuch as frequently the hope of realizing profits will induce individuals to undertake the manufacture of a product, and the attempt may result in failure and consequent loss. The most highly trained and intelligent chemist, if not fully familiar by years of experience with actual cost calculations, is more liable greatly to underestimate a cost than he is to overestimate it.

It may be of interest to recall here one of the useful and constructive activities of the American Dyes Institute. In 1919 a Committee of Cost Accountants was appointed by the American Dyes Institute for the purpose of formulating uniform cost accounting methods, and the report of this Committee was made and printed in a most interesting pamphlet in February 1920. To quote from this pamphlet:

> One of the most difficult and important questions to be considered in the dye and chemical industry is the proper application of depreciation, obsolescence and maintenance as elements of cost.
>
> In the dye industry obsolescence assumes a position of paramount importance in relation to costs, and it is essential to have a clear understanding of what is contemplated by the term and a sufficiently high rate set to cover obsolescence as charged against costs to fit the needs of the industry.
>
> Obsolescence means the loss of value of buildings and equipment or other assets, which become useless or partly so by reason of causes other than wear and tear or accident. Some observers feel that an obsolescence charge may be as high as 35 to 40 per cent of the value of the equipment, and in some cases even more, but a very conservative average would be 20 to 25 per cent.

OBSOLESCENCE Obsolescence is an item of cost which is more frequently overlooked than any other and which, therefore, is frequently responsible for failures and inability to pay out dividends. It is this very point which is so frequently overlooked by chemists in general, who recommend the purchase of equipment and expenditures for erecting a plant for the manufacture of an intermediate or dye based on estimates of cost in which obsolescence is omitted. After operating for two or three years more or less successfully, the owner realizes that he must either give up the manufacture or adopt a better process, of which he had no knowledge when he undertook the manufacture or which may not have existed then. And so it comes about that honest optimists urge others to invest their money, and after this has been done it often happens that an improved process must be adopted and new equipment purchased before the old equipment has been paid for out of the profits of operation. The chemist, in such instances, is frequently totally ignorant of the damage he has caused, and on the contrary is fully convinced of his great efficiency in having in so short a time so materially improved the manufacturing process as to necessitate a complete change of equipment, without thinking for a second that he has been the cause of great financial losses.

---

[1] Presented before the Section of Dye Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

This obsolescence cost should be emphasized at this time because our industry is in a period of development necessitating frequent changes in process and equipment to such an extent as to affect our profits materially, whereas Germany has to a great extent gone beyond this period of development and its industry has become far more stabilized.

DEPRECIATION—Depreciation is the decline in value of buildings or equipment such as may reasonably be expected to occur as a result of wear and tear, and is continuous.

Depreciation on buildings in chemical plants may be from 3 to 10 per cent depending on the type of construction. Depreciation on equipment in chemical plants may average from 10 to 20 per cent per year, but may in some instances run as high as 50 per cent.

IDLE PLANT CHARGES—Another very important factor of cost is the increase in cost of manufacture due to stoppage in manufacture, which we will call "idle plant charges." Such a stoppage may be due to fire, improvements or changes in machinery or in process, strikes, accidents, shortage of raw material, decrease in sales, or drop in prices. Interruptions of manufacture are far more frequent than would appear at first sight and are naturally part of the cost of manufacture and can be charged either to overhead or manufacturing expenses depending on circumstances.

INSURANCE AND TAXES are naturally higher to-day than they ever were, and therefore are comparatively important items of cost.

As the result of inflated war values all of the above-described elements of cost are themselves inflated and make up a substantial percentage of cost figures. The writer has had an opportunity to compare the item of depreciation in the cost of manufacture of products which he manufactured prior to 1914 with the corresponding depreciation in 1921. On an average of six products, the depreciation item was in 1921 exactly twice the amount charged in 1914, figured on the same basis of 100-pound production. This increased depreciation resulted from the necessity of rebuilding new plants during the war, either on account of changes in process or of increased demand.

Unwise Duplication of Effort

The subject of costs may be apparently foreign to matters of interest to the Dye Section of the American Chemical Society. Realizing, however, that the future development of the American dye industry is dependent not only on the ability of our research and manufacturing chemists but also on their commonsense and on their ability to take a broad view of the situation, it has seemed to the writer that the question of costs should be of general interest.

It is a fact that we have during the last few years forged ahead in leaps and bounds, we have developed our plants without question or hesitation, we have undertaken the manufacture of innumerable intermediates and dyes without paying very great attention to the activities of our neighbors or competitors, frequently without exact knowledge of the market requirements. It seemed that the possibilities of development knew no limits. Our dyes found a ready market and we increased our plants to supply more goods, which in turn were sold as fast as produced, until all at once we struck a stone wall, and we began to wake up to the reality. The 1920 Dye Census tells us the tale.

Some of the data furnished by the Tariff Commission, showing how many manufacturers have reported the production of the various intermediates and dyes are quoted below:

Intermediates	Number of Manufacturers
Acetanilide, technical	9
1-Amino-2-naphthol-4-sulfonic acid	13
1-Amino-8-naphthol-3:6-disulfonic acid	13
p-Aminophenol and hydrochloride	10
Aniline oil	14
Benzaldehyde	8
Benzidine base	9
Benzoic acid, U. S. P. & technical	8
Dimethylaniline	7
Dinitrotoluene	11
2-Naphthol-3:6-disulfonic acid	16
Nitrobenzene (Oil of Mirbane)	9
Nitrosodimethylaniline	11
m-Phenylenediamine	15
Salicylic acid, U. S. P	9
o-Toluidine	8
Dyes	
Butter Yellow	9
Alizarin Yellow GG	11
Alizarin Yellow R	10
Orange II	12
Fast Red A	12
Salicine Black U	14
Agalma Black 10 B	16
Bismarck Brown	11
Benzo Blue 2 B	14
Benzopurpurine 4 B	11
Direct Deep Black E W	14
Magenta (or Fuchsine)	12
Methyl Violet	9
Alkali Blue	10
Sulfur Black	12
Sulfur Blue	9
Sulfur Brown	15
Sulfur Green	10
Eosin Lakes	31
Lithol Red	26
Red Lakes	35

A word to the wise is sufficient. The Tariff Commission has said the word and now the question arises: Are we wise? Are we going to organize our industry in such a way as to eliminate unnecessary duplication of effort. Are we going to concentrate our energies on doing a few things *well* or are we going to attempt *each of us* to manufacture all the chemicals we need, independently of whether we do so efficiently or not?

Have not our manufacturing plants up to this day, and some of our large plants in particular, adopted the policy that their salvation depends on their ability to manufacture all crudes, intermediates and dyes, rather than to permit others to supply one or the other of the intermediates required? We would be far better off if one small manufacturer produced all the *p*-nitroaniline required by our industry than if this product were manufactured independently by three large concerns as the tail end of their plants, because the small manufacturer will give his only product more attention and will probably operate more efficiently, and can serve several large plants at one time.

As an illustration of the various points referred to, the following table, taken from actual manufacturing figures, shows the various items of cost in the production of a fairly important intermediate.

This table illustrates a plant designed to produce 1,200,000 pounds of the intermediate. It is seen that the indirect manufacturing expenses, which include obsolescence, depreciation, etc., amount to 18 per cent of the total cost of the product. Let us assume that a second plant decides to take up the manufacture of this same intermediate, aiming to supply the full market requirements. After some more or less unpleasant experiences and losses, this new manufacturer succeeds in supplying one-half of the demand and therefore produces 600,000 pounds yearly. What is the result? The cost of production of both manufacturers is now 47.68 cents instead of 40 cents per pound, because both plants are working at one-half capacity and the indirect expenses have increased from 18 to 30 per cent of the total cost. If two other manufacturers plan to obtain for themselves the full market the result may be that all four manufacturers will be producing, and therefore the cost of production will increase to 54.59 cents, the indirect expenses having increased to 40 per cent of the total cost.

	Total Cost	I Cost per Lb. Cents		II Cost per Lb. Cents		III Cost per Lb. Cents	
Production, pounds		1,200,000		600,000		300,000	
Raw materials	$248,420	20.71		20.71		20.71	
Direct mfg. expense	108,620	9.00		9.00		9.00	
Rent taxes, insurance	9,120	0.76	X_1	1.62	X_2	2.28	X_3
Depreciation, 15 per cent	30,000	2.50		5.00		7.50	
Obsolescence, 15 per cent	30,000	2.50		5.00		7.50	
Interest, 6 per cent	12,000	1.00		2.00		3.00	
Other indirect expense	6,000	0.50		0.75		1.00	
General admin. expense	7,920	0.66		0.66		0.66	
Selling and shipping	35,640	2.97		3.00		3.00	
		40.00		47.68		54.59	

Indirect Expense

X_1— 7.26 cents, 18 per cent of total cost
X_2—14.27 cents, 30 per cent of total cost
X_3—21.28 cents, 40 per cent of total cost

It may appear that this is an exaggeration, but it is a characteristic illustration of what has happened frequently in this country during the last few years. We have in the United States three manufacturers with a producing capacity of over 2,000,000 pounds of the intermediate referred to in the above illustration and a consumption of less than 600,000 pounds yearly; yet a fourth large manufacturer is seriously contemplating taking up the manufacture of this article. You no doubt realize that our industry is overexpanded in many lines. If it must live on the domestic trade alone, it is high time that we call a halt and begin considering our industry as a whole and not only certain individual units.

There are men with brains, there is energy and determination in every large organization in our industry, and no one organization can claim to monopolize these essentials for success. Our efforts should be directed toward coördination in our industry, for some day we shall face a competitor who knows coördination and elimination of ruinous duplication. If we do not learn our lesson now, our industry will unquestionably suffer later.

Summary

1—We are unable to meet German competition as to costs and are therefore rapidly losing our foreign trade in coal-tar chemicals.

2—Contributing to high costs, outside of wages and other well-understood elements, are other factors such as obsolescence and depreciation, idle plant charges, etc., which are not usually sufficiently recognized by most chemists but which are to-day important items of costs because they are necessarily still figured on the basis of high war values.

3—We have to-day much duplication of effort in our organic chemical industry which still further adds to the burden of these indirect expenses. The consequence of duplication is overexpansion, inasmuch as we attempt to operate four plants where two could take care of our requirements. This condition doubles the depreciation, obsolescence, and idle plant charges.

If such are the existing conditions, what is the remedy?

Much can be said in discussion of what we should do, but it is needless at this time to discuss details which can be easily worked out, provided we recognize the necessity of a change in policy.

What we need is a different mental attitude. We must stop spreading out horizontally and instead we must dig deep down to establish better foundations. This new mental attitude which we must adopt is one of effective coöperation between American manufacturers, and it is necessary that chemists themselves adopt this mental attitude of coöperation, as they are and must be dominating factors in shaping the future of chemical industry of this country. By our intelligent advice and interest, manufacturers will be assisted in abandoning our war-time methods and will adopt a healthier plan of development, taking into consideration, first of all, the needs of our national industry. Instead of encroaching on fields already fully covered in order to satisfy local conditions or personal ambitions, the chemist can, where there is a desire to expand, lead the way towards virgin or neglected fields, of which there are still so many in this country. By so doing you will have done your bit towards minimizing a serious evil threatening our industry.

SOCIAL INDUSTRIAL RELATIONS

Food and Shelter

By H. W. Jordan

Syracuse, N. Y.

Food and shelter absorb from 70 to 90 per cent of the living expense of 85 millions of our 100 million people. Food originates from agriculture. Shelter, which is clothing, housing, and furniture, is in large part textiles, wood, and leather grown from the land.

As wages and salaries are consumed mainly to provide these essentials of life, the most effective way to maintain low cost production in the chemical and engineering industries, and in all industry, is to secure low cost production and distribution of these primary essentials while maintaining equable profit to producers and distributors of them. Maintenance of efficient agriculture and forestry is infinitely more necessary to engineering industry than a tariff.

The extraordinary growth of the United States was founded on free land, cheap food, and ample shelter. Present social discontent and spread of confiscatory ideas spring from increasing cost of food and shelter. Distress of city unemployment is intensified by complete separation of the great majority of our people from direct contact with the land, and their consequent inability to provide food and shelter by their individual labor at the very source of these necessaries of life.

In the period of village or small city industry, a depression in manufacture was not serious. The surplus workers went back automatically to the farms where there was plenty food, fuel, and housing. The normal reaction of depression that followed the Civil War was readjusted by flow of the unemployed to the Eastern farms and the free lands of the West. Little money was in circulation, but there was plenty food, fuel, and shelter back home on the farm.

In 1921, with a large proportion of manual and mental workers city born, with no home ties in the country whatever, and with money from wages or salary the only means of getting the essentials of life, the industrial worker, whether machine tender or chemist, soon becomes resentful when unemployed. He finds himself a product and victim of a complex economic system which caught him young and taught him only one or two narrow, special ways of earning his living. His condition is a result of applied science and of modern, specialized industrial efficiency.

THE LAW OF SPECIALIZATION IS AT WORK UPON HIM. Extreme specialization has led to such lack of adaptability that his chances of survival are greatly diminished unless he returns to a more generalized type. Accordingly, in many cases, he reverts to the primitive occupation of buying and selling. But he stays in the city, because the country offers no appeal to him.

HOUSING IS AN EXAMPLE OF THE ACTION OF MODERN INDUSTRY. New England, New York, Michigan and all the industrial states had extensive timber areas fifty years ago, from which lumber was produced every winter in such abundance that a substantial house to shelter a family of five or six could be built for $2500 from lumber that grew within ox haul. Wood for home fuel was equally cheap and plentiful. Building lots cost little, because free land in the West held down the price of all land.

In 1921 such a home costs $5000 to $8000 chiefly because Eastern lands are stripped of forests, and lumber for houses comes from Oregon, Arkansas, or Georgia. The freight on it is more than the cost of the dressed lumber at the Oregon sawmills. Our annual freight bill on lumber from distant sources exceeds half a billion dollars. Wood for domestic fuel is not to be had at all. Home wood lots are as extinct as the buffalo. Building lots have multiplied in price.

SIMILAR CONDITIONS PREVAIL WITH FOOD. City industrial competition has so depleted farm labor that we no longer feed ourselves from nearby land. We import a substantial percentage of beef, wheat, and corn from Argentina and Canada, mutton from New Zealand, butter and cheese from Denmark, potatoes from Scotland, eggs from China, wool from Australia, lumber, pulpwood, and paper stock from Canada and Norway.

Butter, cheese, eggs and other dairy products used to constitute 30 per cent of our food. Now they are only 15 per cent. Although they are the most nutritious and essential foods, and can be produced within motor truck distance of our industrial cities in plenty, they have been replaced by white flour and sugar foods and by tropical fats and fruit that sustain long haul freight charges often in excess of their cost where they are grown. Declining use of dairy foods and excessive consumption of sugar and white flour is a main cause of loss of teeth, diabetes and widespread malnutrition of children.

Industrial employment managers deplore the inefficiency of workmen. Chemical operators are driven to distraction by the stupid mistakes of city born workmen. Frantic attempts are made to Americanize foreign born Slavic and Latin laborers by teaching them English, with a lot of patter about American institutions.

All the while industrial management makes no attempt to maintain or restore the single great influence that typified the former self-reliant American of Northern European stock and Anglo-Saxon speech. That influence was direct contact with the land and the production of one's own food by one's own labor; a process that compels the use of all one's wits.

INDUSTRIAL MANAGEMENT DOES NOT REALIZE that extreme specialization in city industry is producing equally extreme social discontent and economic helplessness of the individual because industrial management has evolved no method of coöperation between the land and city industry. Worse yet, industry has so drained the farms of labor that the farmer is forced to pay excessive wages, competitive with city industrial workers. Formerly he had abundant labor of boys and youths raised on the land, who worked for board and clothes, and a small, but adequate money wage. This low cost labor and the free land in the West made food wonderfully cheap, and so abundant that our exports were mainly food.

Agriculture and forestry cannot compete with city wages. They require low cost labor that must be provided through coöperation with city industry.

ANOTHER IMPORTANT FUNCTION OF THE LAND is that when nations shift from rural to city life, to the extent that the country is distressed for labor, and ownership of the land is transferred to non-residents so that farms with their food production are in the hands of tenants or financially cramped owners, those nations decline in social, economic, and moral influence. Religion dies as the people lose the idealism that springs from the land and close contact with nature. Rome fell under that influence.

The industries of applied science that chemists and engineers have created since 1880 are confronted by that condition. Modern industry has drained the land, the source of food and shelter, of its requisite share of manhood. Industry has conducted no research to coördinate the land with city, factory production. It has reared an entire generation of city born workers who know nothing of the land. Industry has cut itself off from its three most essential raw materials; self-reliant manhood, food, and shelter. And industry is burdened almost to collapse by excessive wages, taxation, and public charity costs that are part of the reaction from neglect of the land. The unemployed are on the payroll of industry even though the books show no charges to that account.

SUCCESSFUL INDUSTRIAL MANAGEMENT IN THE TWENTIETH CENTURY will be guided by the fact that the greatest profits to industry come from minimum cost of food and shelter that leave a margin of 40 per cent or more from which to accumulate new capital by personal thrift, and upon which to build and maintain superior standards of living. The superficial and gross public spirit that manifests itself by indifference to secondary education, by decline in the drama and rise in jazz, by mediocrity in political leadership and falling influence of religion is in large part the reaction from high cost food and shelter with too small a reserve for expression of the practical high idealism that differentiated America from other nations—the idealism that made America the biggest and best market in the world for manufactured goods.

Scientific physical and chemical research to evolve great industrial plants, new machines, and new processes has subsided. That early phase of industry is drawing to a close and is becoming routine. The great industrial research problems of the twentieth century must be those of human relations. Foremost among these will be the vital task of coördinating the land and its production of food with the applied science of city industry.

Are there no creative industrial executives, no forward looking men who see this vision? The task must be undertaken by the chemists and engineers to bring out creative leaders and engineering statesmen who will apply science to commerce, economics and government as they have applied it to industry. As Korzybski has said, "Neither engineers nor scientific men have any right to prefer their own personal peace to the happiness of mankind; their place and their duty are in the front line of struggling humanity, not in the unperturbed ranks of those who keep themselves aloof from life."

American Association of Textile Chemists and Colorists

About 150 representative textile chemists and colorists from all parts of the country gathered at Boston during the Textile Exposition, on November 3, and organized the American Association of Textile Chemists and Colorists. The following officers were elected: Professor Louis A. Olney, Lowell Textile School, president; William D. Livermore, American Woolen Co., Lawrence, Mass., and William H. Cady, United States Finishing Co., Providence, R. I., vice presidents; Walter E. Hadley, Clark Thread Co., Newark, N. J., secretary; Winthrop C. Durfee, consulting chemist, Boston, treasurer. The following members of the executive council were chosen: George A. Moran, Pacific Mills, Lawrence, Mass.; Walter M. Scott, Cheney Bros., South Manchester, Conn.; A. E. Hirst, American Printing Co., Fall River, Mass.; Elmer C. Bertolet, Philadelphia Textile School; James L. Amsden, Rockland Finishing Co., Haverstraw, N. Y.; W. K. Robbins, Amoskeag Manufacturing Co., Manchester, N. H.

Local sections of the Association are to be formed shortly, embracing the territory adjacent to Boston, New York, and Philadelphia.

A statement of the objects of the Association was printed on page 891 of the October issue of THIS JOURNAL, in connection with the account of the preliminary meeting in New York City in September.

NOTES AND CORRESPONDENCE

A Study of the Fundamental Laws of Filtration Using Plant-Scale Equipment

Editor of the Journal of Industrial and Engineering Chemistry:

Work of the kind described in the paper of the above title, appearing in THIS JOURNAL, **13** (1921), 610, meets with the decided approval of the writer, but he feels obliged to criticize certain statements and conclusions made as likely to produce incorrect impressions.

In the first place a statement is made that the fundamental law of filtration is expressed by the equation

$$\frac{dV}{d\Theta} = \frac{KA^2P^n}{V^m}$$

where V = total volume of liquid filtered; Θ = time; A = filtering area; P = pressure; K = a constant; n = an exponent of P varying with the nature of the solids, and m = a possible exponent of V depending upon the solids.

The writer does not agree with the author here, as no filtration can take place without a filter base, *i. e.*, a porous mass to initiate the process—frequently cloth. In the above equation the effect of the filter base is utterly neglected and it cannot therefore be properly called the fundamental law of filtration. Furthermore, it fails to consider separately the effects of the resistance of the cake, the per cent of solids in the mixture, or the rate of deposition of solids. The effect of these variables are lumped into one constant, K, whereas in a fundamental formula they certainly ought to be separated so that the effect of changing any one of them can be studied.

To show that the formula is not really reflective of actual conditions and hence not fundamental, the writer integrated it, taking $m = 1$ as assumed in the article, obtaining the following expression:

$$V = C\,P^{\frac{n}{2}}\,\Theta^{1/2} \qquad C = \text{constant}$$

Next the writer plotted the 55 lb. per sq. in curve shown in Graph 3 on logarithmic cross-section paper. Now if the equation is correct, the slope of the curve ought to be 0.5. Actually, as will be seen in Curve 1, the curve is not 0.5 nor indeed is it even a straight line. Unquestionably this discrepancy from the equation which is called fundamental is due in slight part to error in observation, but primarily because the equation entirely neglects the effect of the filter base, a fundamental condition of filtration, which is a subtractive quantity, as given in the present writer's formula,

$$V = \sqrt{WP\Theta + N^2} - N,$$

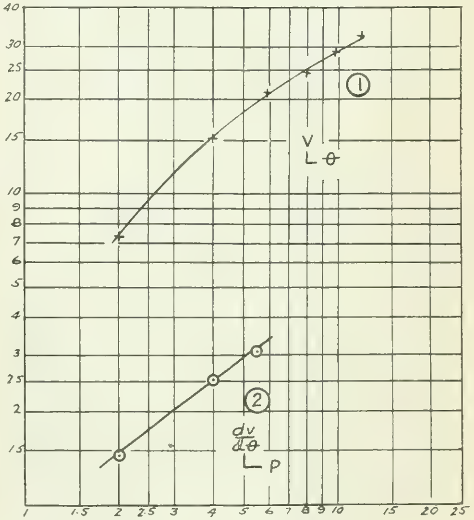
where V = total discharge; P = pressure; $W = \frac{2K}{R\%}$; $N = \frac{KR_m}{R\%}$; Θ = time; K = rate of deposition of solids; R = resistance of the porous mass; % = per cent of solids in the mixture; and R_m = resistance of the filter base.

The effect of the filter base is important and increases in importance as the per cent of solids in the mixture, %, and the resistance of the porous mass, R, decrease, and as the rate of deposition, K, and the resistance of the filter base, R_m, increase.

If a time-discharge curve be obtained from a fine suspension of precipitated calcium carbonate in a liberal amount of water, it will be found that N becomes a very important factor. The writer recalls how puzzling the various curves and slopes of time-discharge curves were until fully explained by the fundamental law of filtration which he later derived, together with the device described in his article appearing in *Met. Chem. Eng.*, **16** (1917), 161.

Baker makes the following statement, referring to the writer's article in *Met. Chem. Eng.*, **15** (1916), 198 (enunciating the fundamental law of filtration): "In the formula which Sperry derives, he takes the exponent of the pressure to be 1.0 in all cases, which, as proved by Lewis and Almy, and by the results described in this article, is entirely erroneous."

That this statement is not true is evident by the last paragraph of my article, referring to the fundamental law of filtration derived in that article, "Two other factors may be added to this list, one, a factor modifying P, the pressure to allow for the squeezing together of nonrigid solids as the pressure increases ......" The fact also that the writer is at the present time, and has been for some time past, doing research work on the effect of pressure on the rate flow of water through nonrigid porous masses, indicates that he was well aware that n was not necessarily unity.



The writer has carefully analyzed the curves shown in Mr. Baker's article, but only after diligent effort, owing to the absence of any log of the observations taken. The conclusion reached that $n = 2$ is in his opinion not correct. Comparison of the constant pressure curves in Graph 3 shows at a glance that this cannot be so. The formula for the total volume as given above is:

$$V = CP^{\frac{n}{2}}\,\Theta^{1/2}$$

In other words, if $n = 2$ and the pressure be doubled, the value of V would also double, providing Θ is kept constant. Drawing a perpendicular line through $\Theta = 64$, it is found that for 20 lbs. per sq. in. V = 150 cu. ft., whereas for 40 lbs. per sq. in. V = 180 cu. ft. If the value of n was 2, the latter should be 300 instead of 180.

The writer also drew a horizontal line corresponding to V = 150 cu. ft. At the points where this line intersects the three constant pressure curves there is obviously the same thickness of cake. The only difference at these three points is the pressure and rate of flow corresponding. If at each of these points a tangent be drawn as accurate as conditions permit, the slope of each tangent measures the approximate rate of flow at that point. If these slopes be plotted on logarithmic cross-section paper against the pressure, then the slope of the resulting line is n. This is true according to the formula:

$$\frac{dV}{d\Theta} = \frac{KA^2P^n}{V^m}$$

because the tangents correspond to $\frac{dV}{d\Theta}$, and $\log \frac{dV}{d\Theta} = n \log P + \log \frac{KA^2}{V^m}$, where V = constant and $m = 1$.

In plotting the slopes and pressures, a value of n less than unity is obtained, in the neighborhood of 0.70 (see Curve 2).

Turning to Graph 2 (Baker) where an effort is made to find the value of n which is finally taken as 2, the writer tabulated the data as well as the small scale of the curve would permit. He found that the data were rather inaccurate. The text states that readings were taken every 5 min., and since the curves are for constant flow conditions the difference between consecutive readings ought to be the same. Actually this is far from being the case. Not only is this true, but furthermore the pressure readings are not uniform; in some cases no change in pressure is recorded for three consecutive readings. I realize the extreme difficulty of trying to cause a filter to flow uniformly and do not believe it can be done with sufficient accuracy to produce results of much value. No effort is made to allow for leakage, or that portion of the mixture which ran through the filter base at the start of the run. This is added in as part of V, a source of error. Another factor neglected is that due to the increased sagging of the filter cloth between supports as the pressure increases thus increasing the filtering area and tending to augment V.

If these curves are plotted with initial conditions, say, at the fifth reading, after the leakage conditions are probably passed, a slope approaching unity is obtained. According to the formula

$$\frac{dV}{d\Theta} = \frac{KA^2P^n}{V^m}$$

there can be no objection to this. The conditions at the fifth reading are the same as though the run started at that point with a filter cloth having a resistance equal to that of the filter cloth plus that of the cake already deposited at the fifth reading.

It is hardly practical to determine factors of a fundamental formula by such crude apparatus as used. Sedimentation has an effect in the filter used which cannot be eliminated. There is also no assurance that the mixture filtered was of the same kind in the various runs. It is stated that the filter surfaces were merely sluiced off between runs; doubtless there was no way to prove that the sluicing was equally thorough in all cases.

D. R. Sperry

119 McKee St.,
Batavia, Ill.
August 13, 1921

Editor of the Journal of Industrial and Engineering Chemistry:

The criticisms in the above letter may be summarized as follows:

1—The filtration law we used is not fundamental because:

(*a*) The resistance of the filter base was not taken into account.

(*b*) It fails to account separately for (1) resistance of cake, (2) the per cent solids in sludge, and (3) the rate of deposition.

(*c*) Because even our own data do not give a straight line whose slope is approximately 0.5 when the log of the volume of discharge is plotted against the log of the pressure.

2—Our quotation from Mr. Sperry's article in *Metallurgical & Chemical Engineering* incorrectly interpreted Mr. Sperry's views.

3—That whereas for the sludge in question we compute n as 2 in the formula

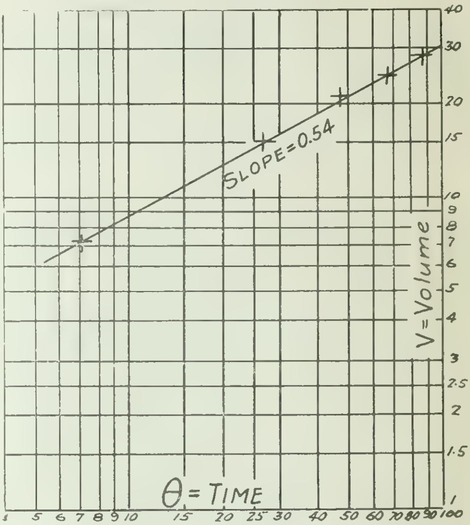
$$\frac{dV}{d\Theta} = K\frac{P^n}{V^m},$$

Mr. Sperry computes it as 0.7.

4—That a tabulation made from our log pressure-log volume plot shows $n = 1$.

5—That in general the formula developed by Mr. Sperry is to be preferred to that developed by Lewis and Almy [This Journal, 4 (1912), 258].

6—That it is impractical to develop a fundamental formula with the crude commercial apparatus used.



We will take up these criticisms in the order named.

1—(*a*) The influence of the resistance of the filter base is important, but only as a resistance in series with the filter cake resistance itself. In view of the severe limitations of present filtration formulas we did not believe this refinement necessary at present. Mr. Sperry is right that the ultimate formula should include this term.

(*b*) Our constant "K" contained the three factors in question for our particular sludge. Here, too, these factors should be separated in the final formula.

(*c*) It is obvious, from Graph 1 and the text, that the formula used does not hold during the first few minutes of a run. It is also equally clear from the same graph that after this preliminary period the volume squared is proportional to the time. Therefore, when the log of volume is plotted against log of time (after this preliminary tare time) a straight line with a slope of 0.5 must result. Mr. Sperry, in his plot, tries to show this mathematical relationship to be untrue, but if the points used by Mr. Sperry are replotted after allowing for the initial tare time of 13 min. (intercept of $V^2 - \Theta$ curve with $V^2 = O$) the conclusion reached from our Graph 1 is confirmed. The plot accompanying this communication is Mr. Sperry's points plotted on the same paper and with the same scales, but with this 13 min. allowed for.

2—The formula quoted from Mr. Sperry's article (*Loc. cit.*) is as follows:

$$dT = \frac{R^{c}{}_{c}Q}{PT}\,dQ + \frac{R_m}{P}\,dQ$$

Certainly in this formula P has an exponent of 1, and hence the rate $\frac{dQ}{dT}$ must have been assumed to vary with the first power of the pressure. Also, in at least three places in the text of the article Mr. Sperry states that the rate of flow varies with the first power of the pressure, as, for example, on page 201 where it is stated, "for the present the proposition that the rate of flow through a filter cake varies directly as the first power of the pressure and inversely as the first power of the thickness must be accepted as true." That the rate does not vary directly with the pressure is shown by experimental results obtained under careful laboratory conditions and published in THIS JOURNAL in 1912.

3—If we assume the filtration law used to have the same coefficients in both constant pressure and constant rate runs and if the values of n in the different runs gave close checks, then Mr. Sperry's method of computing n and ours should agree. However, both of the above assumptions are incorrect. Mr. Sperry's coefficient of $n = 0.7$ applies to the constant pressure runs, whereas our coefficient $n = 2.0$ applies to the constant rate runs. The text referred to $n = 2$ for constant rate runs and the curvesin Graph 2 are labeled "constant rate." Mr. Sperry's method could have been used on the constant rate runs (*i. e.*, for constant thickness of sludge, v, plot log $\frac{dV}{d\Theta}$ against n log P, the slope of the resulting line giving the value of n). When the rates were 158 and 194 cu. ft. per hr., respectively, the points lie too close for accuracy, but even so, this method of calculation indicates n at least equal to 2. In our article the value of $\frac{n}{m}$ for each constant rate run was obtained by plotting the log of pressure *vs.* the log of volume. The three runs gave $\frac{n}{m} = 1.7$; $\frac{n}{m} = 2.1$ and $\frac{n}{m} = 2.3$. From the constant pressure runs V^2 was proportional to Θ and, therefore, $m = 1$, and since in all sludges studied m has had values of 0.8 to 1.0 we took $m = 1$; therefore, n was equal to $\frac{n}{m}$. If m did equal [illegible].8 instead of 1.0 the value of n would be approximately 1.6 instead of 2. What interested us and what we were trying to show was that for constant rate runs n was greater than unity.

4—With respect to the fourth criticism we believe it better to plot all data and draw a representative line than to compare point with point. Graph 2 in our article shows that the points themselves vary and we took the general trend or slope of these points as our representative line.

5—Although not pointed out by Mr. Sperry, the equation which he proposes as fundamental is designed to be applicable only to runs made under constant pressure, and hence is not general. This is true because it is derived by means of an integration in which the pressure P is placed outside of the sign of integration, and the expression integrated, holding P constant. As shown by the tests described in our article, constant rate of flow filtration is fundamentally different from constant pressure and the equation derived for one is not directly applicable to the other.

Further, the real use of a law of filtration should be to afford a means of calculating sizes of filter equipment, which involves an area term. At no place in Mr. Sperry's equation does such an area term appear, nor is it readily apparent how the equation could be translated into terms of area of filtering medium.

It is acknowledged that the equation of Lewis and Almy used in calculating the results of the tests described was derived for constant pressure operation and is not strictly applicable in its present form to constant rate of flow conditions. As a result, important progress is being made in research work to alter the equation so that it will hold for both constant pressure and constant rate of flow conditions. However, the equation as it is holds rigidly for constant pressure runs at different pressures, whereas the equation proposed by Mr. Sperry does not, as can be shown by plotting the data of Lewis and Almy, and determining the constants in Mr. Sperry's equation at various pressures. These are found not to be constant at all for different pressures, when the runs are made with the same sludge under otherwise identical conditions. The equation Mr. Sperry proposes probably holds for incompressible sludges such as sand or kieselguhr, but it will not hold for gelatinous precipitates.

6—In regard to the criticism that our plant tests were made on commercial apparatus of too crude a nature for determining factors of a fundamental formula, I wish to call attention to the fact that we were not trying to determine the formula, as that had been done by Lewis' and Almy years before. We were simply applying the formula to plant-scale equipment for the purpose of testing the application of theory to practice. While we admit that Lewis' equation is not at present complete for constant rate of flow, its simplicity and also its complete applicability to constant pressure conditions made it satisfactory as a starting point for investigations in constant rate of flow filtrations.

That the mathematical treatment of filtration is still undeveloped is apparent when one tries to determine for a given sludge the best filtration method, *i. e.*, the proper thickness of cake and whether the cycle should be at constant pressure or constant rate of flow, together with the proper pressure or rate.

F. P. BAKER

SCHOOL OF CHEMICAL ENGINEERING PRACTICE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
September 6, 1921

The Variability of Crude Rubber

Editor of the Journal of Industrial and Engineering Chemistry:

In a recent paper [THIS JOURNAL, **13** (1921), 519] Mr. J. B. Tuttle describes results of experiments which led him to the conclusion that a simple mixing of rubber and sulfur is not suitable for the purpose of testing the variability in rate of cure of plantation rubber, because (1) the variability shown by such a simple mixture is much greater than that met with in the factory where it is usual to add varying quantities of organic and inorganic accelerators, and (2) because one particular synthetic product is found actually to retard vulcanization except in the presence of zinc oxide, when it acts as a powerful accelerator. The author therefore concludes that all tests on crude rubber should be performed on mixtures to which have been added from 2 to 5 per cent zinc oxide.

As my name is mentioned with others as favoring the simple mixing of rubber and sulfur for testing purposes, I would take the opportunity of pointing out that I have used for some time a mixing containing zinc oxide but of late have confined myself to a simple rubber-sulfur mix for routine testing purposes as I did not find that the presence of zinc oxide had any appreciable effect on the results. Mr. Tuttle will admit that it is only a few powerful accelerators such as the CS_2 condensation product of dimethylamine and homologs, termed by Bruni "ultraaccelerators" which are much influenced by the presence of basic oxides, in particular zinc oxide, and he has not shown that accelerators of this type are present in crude rubber. Unless such are present the addition of zinc oxide is superfluous.

I am in many ways in agreement with Mr. Tuttle's general arguments, in that I consider the basis of the mixture employed for testing should be broadened so as to include ingredients commonly used in the rubber factory. It is however impossible to make up and test a large number of different mixtures for each sample of plantation rubber under examination. Under these circumstances it is wisest to employ the simplest mixture possible, namely, rubber and sulfur only. Moreover, provided a sufficiently large proportion of sulfur is used, this mixture has the advantage that it accentuates variations inherent in the raw rubber. It is consequently more sensitive than mixings containing organic and inorganic accelerators. On the other hand, the almost exclusive use of this simple mixture by chemists in the East has given rise to a false impression as to the variability of plantation rubber, as it has been assumed that variations similar to those found with this mixture would also be experienced with the technical mixtures in the factory. If Mr. Tuttle will refer to my publications he will note that I have carried out many experiments with litharge and other ingredients and have emphasized the importance of a wider basis for raw rubber testing.

HENRY P. STEVENS

15 BOROUGH HIGH ST.
LONDON BRIDGE, S. E. 1
LONDON, ENGLAND
August 4, 1921

....

Editor of the Journal of Industrial and Engineering Chemistry:

Dr. Stevens states that he has tried zinc oxide and did not find it to have any appreciable effect on the results. It will be quite apparent that zinc oxide will eliminate any retarding effect caused by small amounts of acid, and hence cannot fail to have some effect in reducing that part of the variability which is due to impurities in the rubber, and not to variations in the rubber itself.

He is quite mistaken in assuming that it is only a few accelerators, such as the dimethyldithiocarbamates, which are influenced by the presence of basic oxides; some of the weaker accelerators, such as thiocarbanilide, are absolutely ineffective in the absence of basic fillers. In this country, it is an almost universal custom to have some basic oxides present in any compound containing organic accelerators, although there are some with which this is not necessary.

There can be no question regarding the impossibility of using a large number of formulas for testing rubber; one should suffice, and the simpler the formula, the better. However, we must not lose sight of the fact that we are testing the quality of the crude rubber, and not whether or not there are minute amounts of organic accelerators which have been retained during the process of coagulation, etc. Hence, we should use the simplest formula which will develop the facts regarding the crude rubber **only.** If the simple formula of rubber and sulfur would do this, there could be no objection to its use, but the facts are against it. Dr. Stevens' experiments with zinc oxide and with litharge show that he, like many others, has felt the urgent need for some better way of testing crude rubber than by the simple formula of rubber and sulfur. He admits that the almost exclusive use of this formula by the chemists in the East has given rise to a false impression as to the variability of plantation rubber. Well, if the use of this formula by the plantation laboratories produces false impressions, what else can we expect in the laboratories of the consumers? Is it not logical to suppose that they will have as large variations in their crude rubber tests as have been shown by the chemists of the Far East? And when they do obtain these differences, will they not feel a certain prejudice against plantation rubber which may be, and in my opinion is, absolutely unwarranted?

Dr. Stevens has surely compared the rate of vulcanization by means of the rubber-sulfur mixture, of an exceptionally clean, thoroughly washed rubber, with the so-called "slab rubber." The former, containing practically no impurities, will hardly vulcanize at all; the latter, with all sorts of fermentation products, vulcanizes rapidly. A vulcanization test of this type would condemn the former; in other words, we are placing a premium on fermented rubber; on delay in coagulation; on poorly washed rubber; on general carelessness and poor management. In the face of the excellent results obtained in the industry with the use of plantation rubber, we dare not accept the logical conclusion. Obviously there is an error in our argument and equally obviously, the error lies in the means by which we measure quality.

Practically every one interested in the subject believes that there is some variability in plantation rubber (confining our argument to standard high grades only, the poorer grades necessarily are not comparable). I feel, and from what he has written I believe that Dr. Stevens agrees with me, that the amount of this variability is very much less than has been popularly supposed to exist. We have been sticking to an antiquated and wholly insufficient test because of the seeming impossibility of getting a new and better one adopted. Perhaps I did not go far enough in my suggestion regarding the improvement in the testing formula; it might have been better to have included the suggestion that to the rubber, sulfur, and zinc oxide, we add sufficient organic accelerator to cure properly the standard high grades of plantation rubber. There can be no logical objection to organic accelerators; we know that some crude rubbers contain them, and they materially aid in the vulcanization, and to add such an accelerator would merely tend to a greater uniformity. Just which one should be used is a matter which could be decided by the leading plantation chemists. The consumers are in the unfortunate position that by reason of their ignorance as to the manner of preparation, they are unable to make these tests effectively—they must be made at the place where the rubber is prepared. It will be a great step forward if the planters and consumers could get together on this subject and find out the true amount of variability, its causes, and the means for its elimination.

JOHN B. TUTTLE

68 BANK ST.
NEW YORK, N. Y.
August 20, 1921

The Nitrogen Supply of the World

Editor of the Journal of Industrial and Engineering Chemistry:

The nitrogen demand and supply has of late been the subject among us of much thought and discussion. It is indeed one of the most important and far-reaching problems with which the chemist has to deal. For this reason, it has seemed to me worth while to prepare for the benefit of the readers of THIS JOURNAL a brief digest of a recently published German book[1] dealing with this subject.

The title of the book is "The Nitrogen Supply of the World;" the author, Walter Eucken. It discusses the subject solely from the point of view of economics, mentioning only incidentally the chemical, biological, and technical aspects of the subject. The periods before, during, and after the world war are treated in separate sections.

In the section devoted to the pre-war period an account is given of the development, both of the demand for and supply of nitrogen throughout the world. There is also a careful description of the world's nitrogen market as it then existed, including its organization, its method of fixing prices, and the syndicates and cartels which dominated it.

The section devoted to the war period is divided into two parts, one dealing with the situation in Germany, the other with that in allied and neutral countries. The first part is especially interesting to us. The author states that the total German nitrogen supply on hand in April 1914 plus that captured later in Antwerp, Ostende, and northern France amounted to 50,000 tons. In 1913 to 1914 the coke ovens and gas works in Germany produced 110,000 tons, but with the initial slump in the iron industry at the beginning of the war this dropped to 65,000 tons of nitrogen per year. There was a small arc installation (Pauling) at Muldenstein, near Bitterfeld, in the brown coal region designed to operate on off-peak power in peace time, and another similar plant was started at Zschornewitz in the same region in 1915. There was also an arc plant at Rhina in Baden operated by electricity supplied by Swiss water power. In 1917 the plant at Muldenstein had to shut down on account

[1] "Die Stickstoffversorgung der Welt, Eine volkswirtschaftliche Untersuchung," by Walter Eucken. Deutsche Verlags-Anstalt, Stuttgart, 1921. 185 pp. 23.5 × 15.5 cm. Price M. 28. Bound in half linen, M. 35.

of the coal shortage, that at Rhina because of technical difficulties and that at Zschornewitz blew up—so that these installations never made any significant contribution to the nitrogen supply. There were cyanamide plants at Knapsack and Tröstberg with a combined output of 12,000 tons of nitrogen per year, while the Haber-Bosch plant at Oppau had an output of 7000 tons with a new plant under construction which assured a supply of 30,000 tons per year. Altogether, these several sources would furnish something like 110,000 tons of nitrogen per year.

This supply, together with the 50,000 tons on hand, appeared adequate for all the German military requirements. But it was immediately evident that the residue available for agriculture would be wholly inadequate, for in 1913 Germany had used 215,000 tons of nitrogen in fertilizers. Vigorous measures were therefore taken at once to increase the supply of nitrogen. Walter Oswald discovered that the addition of chlorides prevented the decomposition of ammonia at high temperatures in the retorts, and facilitated its condensation; but this advantage was minimized and attempts to increase the supply of nitrogen from this source checkmated by the stagnation in the iron industry and the resultant lessened coke production. The cyanamide plants at Knapsack and Tröstberg were enlarged to furnish 22,000 tons, new plants were erected at Waldhut in Baden to produce 8000 tons, at Pisteritz in central Germany to produce 30,000, and at Chorzow in upper Silesia to produce 15,000 tons, making a total of 75,000 tons of nitrogen per year from cyanamide. The Haber-Bosch plant at Oppau was further enlarged to yield about 70,000 tons and another similar plant was started at Merseburg to yield 30,000 tons of nitrogen per year. These sources, with the 65,000 tons from coal, would give in the early part of 1916 an output of 240,000 tons of nitrogen per year. Estimating the military requirements at 60,000 tons, the residue of 180,000 tons, if not ample, still appeared to be adequate as an emergency supply of nitrogen for agriculture.

But the calculations proved to be utterly illusory. In the first place, the rated outputs because of unavoidable technical difficulties were almost never fully attained. In the second place, the military requirements increased far beyond any expectation. The so-called "Hindenburg program" proposed on August 31, 1916, and soon adopted, required for military purposes alone 240,000 tons of nitrogen per year—or an amount equal to the total rated output!

The Germans redoubled their efforts. The by-product output, thanks to the tremendous metal requirements of the Hindenburg program, would be 100,000 tons per year. The cyanamide plants could be but slightly expanded because of the great coal requirements, but the Haber-Bosch plant at Merseburg was enlarged to yield 130,000 tons, making a total output of 390.000 tons of nitrogen per year. Actually these enormous outputs were not fully realized. The coke ovens and gas plants did indeed produce in 1917 to 1918, 100,000 tons, but the cyanamide plants produced only 66,000 and the Haber-Bosch plants 105,000 tons—or a total of 271,000 tons of nitrogen. German agriculture, which in 1914 took 215,000 tons of nitrogen in commercial fertilizers, actually received in 1915 to 1916, 79,000, in 1916 to 1917, 109,000, and in 1917 to 1918 only 92,000 tons of nitrogen. In other words, in spite of its tremendous expansion, the German fixed nitrogen industry was only able to keep pace with the military requirements, and German agriculture never got more than 40 per cent of its peace-time requirements of commercial nitrogen. Its supply of nitrogen in the form of manures showed a corresponding deficit.

The author points out that this deficiency of nitrogen was one of the most important reasons for the decrease in the productivity of German soil during the war, and was therefore one of the economic reasons for the collapse of Germany. He therefore questions whether the efforts to increase the nitrogen supply, in spite of their magnitude and their success in meeting the immediate military requirements, can be looked upon as successful.

The final section, devoted to the post-war situation and the outlook for the future, both in Germany and outside of Germany, is also of much interest. In Germany, while the population has decreased about 11 per cent during the war the total available human food supply has decreased nearly 40 per cent. This has resulted in a marked increase in mortality in urban population and a marked decrease in industrial efficiency. Importation of foodstuff offers no solution of the difficulty—for it requires an increase in the export of manufactured goods, and this is impossible until adequate nourishment is secured. The only way out is to increase the domestic production of foodstuff and the prime necessity here is an increase of nitrogenous fertilizer. If only the amount corresponding to the consumption in 1913 to 1914 were to be used, 445,000 tons of artificial nitrogen would be required because of the great diminution in the supply of manure. The actual yearly output of the partly completed war plants is put at 310,000 tons of nitrogen—so that, instead of the overproduction which was predicted during the war—there is an acute domestic demand for all the nitrogen which these plants can produce.

The production in Chile, too, in spite of the many technical and economic improvements introduced during and after the war, has shown a marked decline as compared with war and pre-war figures. In the United States there has been a marked increase in the production of by-product ammonia, but this has been balanced by a corresponding decrease in the supply from similar sources in England, Belgium, and France, caused by difficulties in the coal mining industry, difficulties which are but slowly disappearing. On the other hand, the author emphasizes that there must be a marked increase in the demand for nitrogenous fertilizer all over the world as compared with pre-war times because of the greatly increased recognition of its importance. All told, therefore, he sees a world-wide demand for all the nitrogenous fertilizer which can reasonably be produced in the near future.

So far as the relative advantage of nitrogen from cyanamide *versus* that from Haber-Bosch ammonia is concerned, the author states that in spite of the relative cheapness of Haber-Bosch ammonia, because of the high cost of sulfuric acid, cyanamide nitrogen is cheaper in Germany than the nitrogen of ammonium sulfate. He also expresses his confidence that in spite of the disturbing effects of anomalous industrial conditions and depreciated exchange in Chile, German fixed nitrogen will be able to compete successfully with Chile saltpeter at least in Germany after, just as it did before the war.

HARVARD UNIVERSITY
CAMBRIDGE, MASS.
September 6, 1921

ARTHUR B. LAMB

Adoption by the Colleges of Standard Metric Units—Addendum

This paper by Dr. Eugene C. Bingham was presented at the "Special Order on World's Standardization" before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

The investigation of white clays east of the Mississippi River has been practically completed at the Ceramic Experiment Station of the U. S. Bureau of Mines, at Columbus, Ohio. The results indicate that none of the clay samples were similar to English china clay, which under the microscope is seen to be composed largely of plate-like particles, whereas the American clays, particularly secondary kaolins, contain more or less irregular or amorphous particles. The primary kaolins from North Carolina resemble English clay more closely in physical appearance than other clays, but have a much coarser grain and contain more free silica than English clay.

SCIENTIFIC SOCIETIES

Synthetic Organic Chemical Manufacturers Association of the United States

Representative manufacturers of synthetic organic chemicals met at the Hotel Washington, Washington, D. C., on October 28 and 29 to effect a comprehensive national organization of the several closely related lines of manufacture included in this branch of chemical industry.

The name of the new organization is Synthetic Organic Chemical Manufacturers Association of the United States. Its purposes, as set forth in the Constitution adopted, are

> To advance the science of organic chemistry by encouraging the manufacture in the United States of all kinds of organic chemicals; to coöperate with the various agencies of the Government of the United States in its efforts to develop, improve and render serviceable a complete organic chemical industry; to promote cordial relations between American concerns and individuals engaged in the production and use of organic chemicals; to afford means for the dissemination of scientific knowledge; to promote the highest scientific and business standards in relation to the industry; and generally to take such collective action as may be proper for the establishment and perpetuation of the organic chemical independence of the United States of America.

The Association is subdivided into four Sections—Dyestuffs, Pharmaceuticals, Intermediates, and Fine Organic Chemicals, each Section having a vice president, a secretary, and an executive committee.

The administration of the Association is in the hands of a Board of Governors, consisting of the president, the four vice presidents, and ten members nominated by the Sections.

The following officers were elected:

President: CHAS. H. HERTY, formerly editor of THIS JOURNAL.

Vice Presidents: C. N. TURNER, Dyestuff Section; HERMAN SEYDELL, Pharmaceutical Section; S. W. WILDER, Intermediate Section; B. T. BUSH, Fine Organic Chemical Section.

Messrs. R. S. Burdick, R. C. Jeffcott, August Merz, M. R. Poucher, P. Schleussner, and F. P. Summers were elected members of the Board of Governors. The remaining four members, one from each Section, will be elected later.

The president and the four vice presidents are *ex-officio* members of the Board of Governors.

After adjournment Dr. Herty gave out the following statement:

> At last there has been brought together one effective organization of men who, for the past five years, have been developing in this country all lines of manufacture of synthetic organic chemicals. The fine spirit shown throughout the meetings gave assurance of a strong organization which will aid in developing to its maximum efficiency this industry born of the war period and now recognized by all as being of such fundamental importance to the nation.
>
> Much progress has been made, but there is a long road ahead before we can hope to give to our country an industry which can worthily meet its every need. Toward that goal we are facing. The Association as organized is thoroughly democratic in character. It follows national lines in this respect, for in the councils of the Association the small manufacturer has equal voice with the larger and we all recognize that the success of the industry is closely bound up in the welfare of the small manufacturer. There have been some points of friction in the past between producer and consumer, but I believe that the hearty spirit of coöperation is developed which in the end will assure the future of this industry. Personally it seems strange to me to be leaving the ranks of the chemists for those of the manufacturers. For six years I have editorially striven to arouse first the chemist and then our people in general to the importance of developing this industry. The idea is now so clear to all that I feel my best efforts can be given to work with the manufacturers on their many problems in the hope of aiding them in the firm establishment of that industry which is so vitally important to this nation that Secretary Hoover, in his address to us last night, while emphasizing that the main consideration now was the development of this industry for utilization of waste, added: "In these days of the development of forms of warfare that we have to exist under, it is fundamental and vital to us that we should maintain those industries on which we are bound to depend for our very vital existence if we ever come to conflict."

The 1921 Meeting of the Association of Official Agricultural Chemists

About 400 members and visitors attended the annual convention of the Association of Official Agricultural Chemists, which was held at the Washington Hotel, Washington, D. C., October 24 to 26, 1921. The usual reports of referees, associate referees, and committees were presented, as well as a number of special papers. Much new work was reported and the interest manifested in all the sessions was highly gratifying.

Honorable Henry C. Wallace, Secretary of Agriculture, welcomed the visitors to Washington in behalf of his department and expressed the belief that the chemist of the future must contribute even more largely than he has in the past not only to the utilization of surplus crops but to the utilization of waste products of all kinds. Dr. Harvey W. Wiley, honorary president of the Association, postponed an operation on his eyes in order to address the Association and delivered one of his inimitable extemporaneous addresses. He stated that the outstanding feature in the realm of chemistry during the past year was the reception tendered Madame Curie on her recent visit to this country. He called special attention to the progress that has been made in the utilization of human foods for dietary purposes, referring particularly to the recent health exhibit at Cincinnati and the similar exhibit to be held in New York City in November. He indicated that one of the big problems of the agricultural chemist of the future was to produce a greater yield per acre—that there must soon be a reflection of the activities of the Association in an economic sense. He strongly urged upon the Association the importance of expressing all business relations in chemicals in metric units and the Association, in one of its later sessions, adopted the following resolution:

> *Resolved,* that this Association endorses the proposal now under consideration by Congress that after due notice the metric system of weights and measures be made the legal system of the United States and also, to further the introduction of this system, recommends that its members in the purchase of supplies, designate and describe the same in terms of the metric system so far as possible.

Dr. W. F. Hand chose for his presidential address "Tendencies of Recent Research on the Photosynthetic Processes of Plants, giving a short historical account of the discovery of fundamental facts regarding carbon assimilation and a discussion of some of the more important theories and experimental work of recent years.

The work completed this past year affords the chemist who is specially interested in the estimation of small amounts of boric acid two reliable methods which, with little further modification, should meet the requirements demanded. The method which was presented for the adaptation of Clark and Lubs' indicator and buffer solutions to the production of an exactly neutral ammonium citrate should greatly lighten the burden of the chemists making the determination of reverted phosphoric acid. Those interested in the production of precipitated phosphates for use in the fertilizer industry noted with interest the important change in the method of analysis of this class of materials authorized by the Association. Several special papers of importance in the determination of nitrogen, phosphoric acid, and small amounts of potash were received with interest.

The Committee on Vegetation Tests on the Availability of Phosphoric Acid in Basic Slag completed its investigations and the detailed report will be published later in the *Journal of the Association of Official Agricultural Chemists.* The committee declared the Wagner method to be a reliable procedure for measuring the available phosphoric acid in basic slag phosphates and recommended its adoption as the official method of the Association.

A committee of five, consisting of H. D. Haskins, J. W. Kellogg, E. G. Proulx, G. S. Fraps, and R. N. Brackett, was appointed to consider definitions of terms and interpretation of results of fertilizer analyses.

The attendance in the Drug Section was the largest in the history of the organization and the program was the most extensive that has ever been presented. Papers relating to the estimation of arsphenamine, neoarsphenamine, alkaloids, silver and silver proteinates, santal oil, acetylsalicylic acid, peppermint oil, and crude drugs were presented and, in some cases, methods of analysis for these products were adopted.

The following committee was appointed to coöperate with the Revision Committee of the United States Pharmacopeia: L. F. Kebler, H. C. Lythgoe, H. C. Fuller, A. R. Bliss, and W. S. Hubbard.

Senator E. F. Ladd, many years an active member in the Association and at one time its president, was called out of town and was unable to address the Association as planned. By unanimous vote, however, he was elected an honorary life member of the Association, as was also Dr. C. L. Alsberg, former secretary of the Association.

Dr. R. W. Balcom, chairman of the Board of Editors, presented a report of progress showing a very material increase in the number of subscribers to the *Journal* of the Association. He stated that the first edition of the "Official and Tentative Methods of Analysis" had been exhausted and that the second edition was now available for distribution. He called particular attention to the fact that the Association has practically caught up in the publication of its back proceedings and within a very few months will be in a position to print original contributions.

A resolution was adopted urging the Congress of the United States to continue adequate, beneficial legislation until the various chemical industries in this country have become firmly established. The Association further expressed its hearty endorsement of the aims and purposes of the Conference on the Limitation of Armament to be held in Washington, D. C., beginning November 11, and expressed the hope that the highest aims and purposes of the Conference on the Limitation of Armament may be attained.

The following officers were appointed for the ensuing year:

Honorary President: HARVEY W. WILEY *President:* F. P. VEITCH
Vice President: A. J. PATTEN *Secretary-Treasurer:* W. W. SKINNER

Additional members of the Executive Committee are H. D. Haskins and R. E. Doolittle.

The names of members of committees, referees, and associate referees for the year 1922 may be secured through the Secretary. The full proceedings of the convention will be printed in the *Journal of the Association of Official Agricultural Chemists.*

N. A. PARKINSON

BUREAU OF CHEMISTRY
WASHINGTON, D. C.
October 28, 1921

Calendar of Meetings

American Institute of Chemical Engineers—Annual Winter Meeting, Baltimore, Md., December 6 to 9, 1921.

American Association for the Advancement of Science—Annual Meeting, Toronto, Canada, December 27 to 31, 1921.

American Ceramic Society—21st Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922.

Cornerstone Laid for New Cornell Chemical Laboratory

The cornerstone of the new $1,500,000 chemical laboratory at Cornell University was laid by the donor, George Fisher Baker, a New York financier and philanthropist, October 20, 1921. Mr. Baker is 81 years of age and has been for years one of the foremost figures in America's finance and industry and has been interested in Cornell University for a number of years, having given in the past a total of $335,000 to the University for residential purposes, in addition to the magnificent donation of the chemical laboratory.

At the exercises held first in Bailey Hall and later at the site of the new building, President Farrand, the newly elected head of the University, presided. An organ prelude by Professor Quarles was followed by the invocation given by the Rev. President Rush Rhees, D.D., LL.D., of the University of Rochester. President Farrand then introduced Professor Emeritus Edward L. Nichols, former dean of the College of Arts and Sciences at Cornell, who made a preliminary address in which he assured the donor of the new building that "if the chemists and students of chemistry who are to work in this building attain only an average output as measured by the performances of university laboratories in the past, the donor may count on returns from his investment such as no commercial enterprise has ever paid."

Dr. Edgar Fahs Smith, president of the American Chemical Society, then briefly reviewed the development and changes which have taken place in the laboratory during the last 100 years. He traced the gradual expansion of the science of chemistry and predicted a great future for it as a result of the splendid research work that is now being carried on.

The program further included an address by Mr. Charles M. Schwab of the Board of Trustees of the University and an address by Prof. L. M. Dennis, head of the department of chemistry, which included a description of the contents of the box of records to be placed in the cornerstone.

The President, the speakers, delegates from other universities and colleges, trustees and the faculty, then led the procession to the site of the new laboratory. The box of records was deposited within the cornerstone by Mr. H. A. Ley, the builder of the laboratory, after which Mr. George F. Baker, the donor, laid the cornerstone.

The contract calls for the completion of the building 100 weeks from the time the ground was broken, last July, and it is now planned to build the ground floor and the first floor, if possible, this fall.

Local Section Meetings

CHICAGO SECTION

December 16—John Johnston, "University and Industrial Research."

EASTERN NEW YORK SECTION, SCHENECTADY

December 9—E. Newton Harvey, "Animal Light."
January —Saul Dushman, "The Quantum Theory."

WESTERN NEW YORK SECTION, BUFFALO

December 20—E. F. Smith.
February 21—A. D. Little.
March 7—E. E. Slosson, "Popularization of Science."

MARYLAND SECTION

December 8—(Joint meeting with A. I. C. E. convention).
J. C. W. Frazer, "Oxidation of Carbon Monoxide to Dioxide at Room Temperatures by a Catalyst."
R. W. Wood, "Ultraviolet Light."

NEW YORK SECTION

December 9—Discussion of Editorial Policy, J. I. E. C.

Honorary Members of the American Chemical Society

At the recent meeting of the AMERICAN CHEMICAL SOCIETY Sir William J. Pope and M. Paul Kestner were elected to honorary membership in the SOCIETY. The following letters of acceptance have been received:

The Chemical Laboratory
The University, Cambridge
30 September, 1921

THE SECRETARY,
THE AMERICAN CHEMICAL SOCIETY,
WASHINGTON.

DEAR MR. SECRETARY:

In electing me one of its Honorary Members the American Chemical Society has done me a great honour and one which I very deeply appreciate.

During my seventeen years membership of the Society I have always been keenly interested in its work and have watched with admiration the rapidity with which it has become, under wise and vigorous management, the largest and one of the most useful chemical organizations in the world.

Whilst asking you to convey my thanks to the Society for the signal distinction conferred upon me may I express that hope that the American Chemical Society may continue its rapid development and become an even more efficient medium for cementing the interests of English-speaking chemists.

Believe me, Dear Mr. Secretary,
Yours very sincerely,
(*Signed*) WILLIAM J. POPE

....

38 Rue Ribiera, Paris
15 October, 1921

MR. CHARLES L. PARSONS,
AMERICAN CHEMICAL SOCIETY.

DEAR MR. SECRETARY:

Your intimation that the American Chemical Society has done me the signal honour of electing me as one of its few honorary members has afforded me the very greatest pleasure and I beg of you to convey to your President and Council the expression of my very sincere thanks.

I am the more sensible of the honour done me in that I feel it to be connected with my association with the Société de Chimie Industrielle. My colleagues in our Society share with me my gratitude for the honour you have bestowed on their president.

It was a matter of keen regret to me that I was unable for a variety of reasons to come over and take part in your annual meeting last month. I had looked forward with much pleasure to making this trip and to seeing you and many of my American friends once more.

Believe me,
Yours sincerely
(*Signed*) PAUL KESTNER

An Englishman's Impressions of the New York Meeting

Because of the international scope of the New York meeting of the American Chemical Society with the Society of Chemical Industry, it is of particular interest to note the impressions of our foreign guests. The "Impressions of an English Chemist" printed in the *Chemical Age*, London, October 8, evidently reflect the thoughts of a number of the foreign visitors to the 62nd Meeting of the American Chemical Society.

The English chemist was favorably impressed with the extent of the membership of the American Chemical Society and the large percentage of this membership which attended the meeting. The splendid recognition given the proceedings of the Society in the public press likewise drew favorable comment from the English visitor. He states that because of the excellent organization of the A. C. S. News Service "the American receives doses of scientific knowledge at regular intervals; he finds it not unpleasant, reads it, and so becomes reasonably well informed on such matters." The writer further observes that the American chemist enjoys a more exalted state in the public mind of the average American and in the minds of his employers, than is the case in England. He observes that "In America, the term chemist means something and it is a name to be proud of for it ranks high in the professions; in England it might mean anything, for the general public knows no better." The writer then comments on the extent to which publicity has been developed for the American chemist and on the fact that the tendency is perhaps to make the level of chemical thought exchanged a little less profound than one expects at scientific meetings and "one could not help but feel that some of the speakers had their eye not so much upon their chemical audience as upon the outside public."

He sums up the source of influence of the American Chemical Society as lying, first, in its complete membership, second, in the high character of its officers, which include men of worldwide reputation in both academic and industrial circles, and, third, in the splendid publications of the Society.

In discussing the scientific aspects of the meeting he brings out the importance given to chemical warfare in the proceedings of the Society; the recognition of the close connection between the organic chemical industry in peace times and the manufacture of munitions and gases in time of war. He also calls attention to the deep thought that is engaging American chemists along the line of supplying substitutes for the energy now being derived from rapidly disappearing natural resources, such as petroleum, gas, coal, etc. It is a healthy sign in the opinion of the writer that Americans recognize the fact that they have exploited nature's gifts rather ruthlessly, and he feels that it should be a source of pride to Americans that the sins of the past are being confessed, and steps taken to secure better treatment for those natural resources which as yet remain untouched. The concluding paragraph of the writer's impressions or observations is of special interest:

> It is still possible to get rich quick in America, and the American is virile, active and as eager for riches as any other man. He is, however, prepared to work for them; he lives nearer to nature than we do and thinks very keenly about his great country of which he is so justly proud. This and that requires to be done, and until it is done there can be no rest, for as he so often says, "We are a young country yet."

Plant Excursions, New York Meeting

As chairman of the Excursion Committee during the recent joint meeting of the American Chemical Society and the Society of Chemical Industry, I wish on their behalf to express my appreciation to the management of the many industrial concerns who so generously extended their hospitality to members and visitors of the above Societies

The spirit of coöperation shown by the management and operating staff of the plants visited aided in no small measure in making the meeting the success it was.

Tours of inspection were made through the following plants:

Seaboard By-Products Coke Co., Jersey City, N. J.
Joseph H. Wallace & Co.. Stamford, Conn.
The Westport Mill, Westport, Conn.
National Lead Co., 135 Marshall Street, Brooklyn, N. Y.
Ward Baking Co., Pacific Street, Brooklyn, N. Y.
Corn Products Refining Co., Edgewater, N. J.
Astoria Light, Heat & Power Co., Shore Road, Astoria, L. I.
American Tobacco Co., 337 W. 27th St., New York City.
Ladew & Co., Lincoln Highway, Newark, N. J.
General Leather Co., Frelinghausen Ave , Newark, N. J.
Ziegel Eisman & Co., Newark, N. J.
National Biscuit Co., 10th Ave. & 15th St., New York City.
Liebmann's Sons, 36 Forrest St., Brooklyn, N. Y.
Tiffany & Co., New York City.
Manhattan Rubber Co., Passaic, N. J.
Toch Bros., 59—9th St., Long Island City, N. Y.
American Sugar Refining Co., Brooklyn, N. Y.
Keuffel & Essel Co., Hoboken, N. J.
Standard Oil Co., Bayonne, N. J.
Balbach Smelting & Refining Co., Newark, N. J.

J. V. N. DORR

Chemistry and Disarmament

Under this general heading three splendid contributions were made to the program of the New York Section of the American Chemical Society, the American Section of the Society of Chemical Industry and the New York Sections of the American Electrochemical Society and the Société de Chimie Industrielle at a joint meeting held in Rumford Hall, New York, November 18, 1921.

All doubt as to the effectiveness of the airplane with its weapons of explosive and poison gas bombs over the battleship was dispelled by the showing of the official U. S. Navy motion pictures of the bombing and sinking of the Ost Friesland, a former German cruiser, and the U. S. S. Alabama.

These pictures were supplemented by an address by Major H. S. Kimberly, formerly of the Chemical Warfare Service.

No one who saw these remarkable pictures can doubt that the day of the battleship is over and that, as Mr. Francis P. Garvan later stated, "the future safety of the nation depends upon the development of airplanes, and a chemical industry which in time of war can be quickly turned into a source of munitions and poison gases."

Both Mr. Garvan and Mr. H. E. Howe, who spoke on "Chemical Research and Business," pointed out the necessity for reiteration of the story of chemistry to the people of the nation, by chemists themselves.

WASHINGTON LETTER

By Watson Davis, 1418 Rhode Island Ave., Washington, D. C.

The Conference on Limitation of Armaments

Washington is now discussing the battleship-limiting bombshell with which Secretary Hughes inaugurated the Washington Conference on the Limitation of Armaments yesterday.

This plan for cutting the navies of the United States, Great Britain, and Japan, which will scrap 66 capital ships and which will save approximately $375,000,000 in construction and upkeep for the United States alone during the ten-year holiday, will result, if adopted, in bringing chemical warfare and the use of aircraft into greater prominence. This is the current opinion here.

Naval armament limitation is without a doubt the most important step planned for the conference, and the success of the other steps in the agenda is largely dependent on the fate of this first proposal. The second topic under "Limitation of Armaments" in the official agenda is "Rules for control of new agencies of warfare," and it is under this head that the discussion of chemical and aerial warfare will come. It is not expected now that the conference will begin to discuss these matters for at least a week or ten days, perhaps not before this letter appears.

The American delegation to the conference has selected an advisory and technical staff to aid them in the various problems of the conference. Herbert Hoover, Secretary of Commerce, is the only technically trained member of the advisory committee of twenty-one members, but included on the technical staff are: Dr. Edgar F. Smith, president of the American Chemical Society; General C. C. Williams, chief of Ordnance; General Amos A. Fries, chief of the Chemical Warfare Service; General George O. Squier, chief of the Signal Corps; William S. Culbertson, United States Tariff Commission; Dr. S. W. Stratton, director of the Bureau of Standards; Dr. J. H. Dellinger, chief of the radio investigations of the Bureau of Standards; L. W. Austin, radio specialist, Navy Department. It is understood that most of the advisory work in connection with chemical warfare will be in the hands of Dr. Smith, General Fries, and army and navy officers.

If the reduction in naval armament is accomplished and chemical and aerial methods come into the foreground, it is pointed out that the world will be adopting methods of warfare that are best suited for defense. Aggressive warfare between nations separated by more than 200 to 300 miles of water is difficult without battleships. Airplanes spreading gas can operate most effectively for only 100 to 200 miles from their base, but for defensive purposes this distance would be ample. From the standpoint of economy, there is hardly any comparison between the old and new forms of warfare.

The question of electrical communication will also be considered by the conference. This will include land telegraphs, cables, and radios. Of these, wireless will hold the most important place. It is entirely probable that at least a good beginning toward definite rules regulating international radio communication will be made. The work is expected to be in the nature of the continuation of that of the recent Paris conference.

Extension of Emergency Tariff Law

Uncertainty as to the present emergency tariff law and the dye licensing provision has been cleared up by the action of the Senate Finance Committee, which has agreed to the House resolution extending this measure until February 1 or until such time as the permanent tariff schedules are enacted into law. Hearings on the agricultural schedules of the permanent tariff bill are planned during the coming week.

The Tax Bill

The tax bill is now out of the Senate and in conference with the House Committee. The tax on nonbeverage alcohol diverted to beverage purposes, which would have been collected on all alcohol and refunded upon proof of legitimate use, has been eliminated, although high taxes for nonbeverage use are provided. The objectionable "guilty until proved innocent" provision would have tied up a large amount of capital for chemical and drug manufacturers. The tax bill as it came out of the Senate has two provisions, both of which double the tax on nonbeverage alcohol or medicinal liquors if they are illegally used. If whiskey and alcohol used in making official preparations or in chemical manufacture find their way into illegal hands, the tax may be as high as $25.60 a proof gallon.

Muscle Shoals

Mr. Ford's negotiations for Muscle Shoals have reached the point where Secretary of War Weeks and Mr. Ford, with their experts, are discussing details. The Secretary of War recently made an inspection trip to the nitrate plant and power plant projects. On November 18 there will be a personal conference between Mr. Ford and Mr. Weeks. As Congress must give the War Secretary specific authority to sell or lease any public grounds, any agreement they reach must be ratified by Congress.

The Journal of Industrial and Engineering Chemistry

Washington chemists are looking forward to the establishment of the editorial offices of the *Journal of Industrial and Engineering Chemistry* in this city, and they will welcome in his new job as editor Mr. Harrison E. Howe, who has been here as resident chairman of the Division of Research Extension of the National Research Council.

Dr. Chas. H. Herty, who has resigned as editor to become president of the Synthetic Organic Chemical Manufacturers Association of the United States, which was organized in Washington last week, carries with him the appreciation of Washington chemists for his work in bringing the *Journal* to its present high plane, and he has their hope for as much success in his new position as with the *Journal*.

The Washington Section of the A. C. S.

The Washington Section of the Society held its annual election of officers on November 10 with the following results: Dr. R. C. Wells, of the Geological Survey, president; J. B. Reed, Bureau of Chemistry, secretary; H. W. Houghton, Hygienic Laboratory, treasurer; Dr. W. D. Collins, Geological Survey, Dr. R. B. Sosman, Geophysical Laboratory, Dr. W. W. Skinner, Bureau of Chemistry, Dr. W. M. Clark, Hygienic Laboratory, Dr. William Blum, Bureau of Standards, retiring president, councilors; C. W. Bacon, Bureau of Plant Industry, V. K. Chesnut, Bureau of Chemistry, Dr. L. H. Adams, Geophysical Laboratory, F. C. Cook, Bureau of Chemistry, C. O. Appleman, University of Maryland, R. O. E. Davis, Bureau of Soils, members of the executive committee.

The Society portrait of Joseph Priestley, discoverer of oxygen and pioneer American chemist, was presented to the National Museum on October 25 by President Edgar F. Smith, at a meeting arranged by the local section. Dr. Charles D. Walcott, secretary of the Smithsonian Institution, accepted the portrait on behalf of the Museum. Dr. F. W. Clarke told of the formal founding of the American Chemical Society at Priestley's former home in 1876.

Corrosion of Buried Pipes

An extensive investigation of the corrosive action of soil on pipes used for gas and water mains and service pipes has been undertaken by the Bureau of Standards of the Department of Commerce. The Bureau has the coöperation of the Bureau of Soils, the pipe manufacturers, and the public utilities through the Research Subcommittee of the American Committee on Electrolysis.

Forty locations have been selected as representative of the principal families of soils to be found throughout the United States and at each will be buried a number of samples of every kind of iron and steel pipe in commercial use. These field tests will be supplemented by laboratory tests which will give complete data on the physical and chemical properties of the soil and on the microstructure, complete metallurgical history, and chemical analysis of the pipe specimens.

It is expected that the experiment will continue for eight or ten years.

Hearings are being held before the House Committee on Rivers and Harbors on bills to prevent pollutions of waters in rivers and harbors. Manufacturing chemists have urged that before steps were taken that would interfere with a large number of manufacturing plants the Secretary of Commerce be requested to conduct a scientific investigation into the causes of water pollution.

The Geological Survey has made public the report on the superpower system. This system would link up power plants and industrial plants 150 miles inland from Boston to Washington and form a gigantic electrical system that would bring about economies in power production and utilization. It is estimated that the superpower system would save annually 4,024,800 short tons of coal for chemical and metallurgical industries alone.

The National Research Council has issued a list of "American Research Chemicals," compiled by Dr. C. J. West.

November 13, 1921

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

The Meeting of the Société de Chimie Industrielle

Without having the same breadth as that of its American sister, the first meeting held by the Société de Chimie Industrielle has been a success, and the exposition which was held at the same time, although limited to dyes and laboratory materials, attracted a great number of exhibitors, a fact which augurs well for the future. The different sections of the meeting heard numerous interesting communications, purely technical, and the special meetings which were presided over by different ministers or under-secretaries of the State brought together a considerable audience where all the social elements were mingled to hear eminent masters open up new horizons on possibilities of the utilization of chemistry. These meetings have had a prolonged echo in the daily press.

The importance of the nitrogen problem, which was treated in all its aspects, has not escaped the attention of the French public who realize all that France owes to her agriculture and all that she ought to do to aid it.

As a matter of course, the lecture of Mr. Claude attracted very great attention. This lecture was given in the great amphitheater of the Sorbonne which holds more than 3000 persons. The amphitheater was full to bursting and 2000 people could not get in, so that Mr. Claude had to repeat this same lecture two days later.

In addition to his researches on ammonia, Mr. Claude developed his ideas on scientific research in general. He recalled the history of certain recent discoveries such as that of invar, that of radium, that of ammonia synthesis, the direct result of Gibbs and LeChatelier, and with these as examples, he showed the infinite variety of resources of scientific research. He insisted especially on the necessity of very attentive observation of all phenomena. In science, he said, there are no phenomena, however small they may be, which can be neglected. How many scientists have passed by great discoveries by not having pushed to their furthest limit the results of a very slight phenomenon. Is it necessary to recall that a French physicist spent several years of his life in establishing the fact that the nitrogen of the air had a density different from that of nitrogen made from ammonium nitrate? Not having carried through to the end the conclusions from this observation he missed the discovery of argon, which Ramsay isolated and characterized only a short time afterward.

Along another line, new and bold ideas of the trend of organic chemistry were developed at the meeting, and I would lay special emphasis on the last point which was treated in a masterly fashion by Sir William Pope, great chemist as well as great traveler, since we received him in Paris at the moment when he returned from attending your meeting in New York, and he has now left us to go toward the Indies.

Sir William Pope showed us that chemistry involving high potential energy has had its day. If all the efforts which have been made to accomplish the synthesis of indigo or that of camphor by purely chemical means had been directed toward the improvement of the culture of the indigo plant or the camphor tree, the yields would have been greater and, moreover, the energy in the coal or the petroleum would have been conserved. The mineral fuels existing on the globe are becoming exhausted slowly but surely. Solar energy, on the other hand, seems to be always available. Therefore, it is toward photosynthesis, in its most general sense, or rather toward the study of the intimate mechanism of the chemical phenomena of life, that we must turn our efforts. There will always be growing in the ground plants which can furnish us with oil. This oil will be a fuel which will renew itself each year, while the oil which we draw from the earth becomes exhausted, and what is true in this case can be applied to many other absolutely necessary products. This program which Sir William Pope outlines for us is evidently only a rough sketch, but each of us can draw the conclusions from it.

Another revelation of the meeting was the important place occupied by motion picture films. The committee in charge of the meeting were inspired with what had been done in the United States and tried to bring together some educational films. Unfortunately the films which were requested from the Bureau of Mines in Washington could not be sent to France where they would certainly have been as successful as the French films which were used.

Beside the films which permitted the audience to see the latest industrial processes for the manufacture of glass, cement, potassium, paper, etc., and the presentation of films which were accompanied by technical papers, a communication was devoted to the use of the motion picture as tool in the hands of the commercial traveler. A small machine, the size of a suitcase, will permit projecting on a 25 × 25 screen a film showing the operation of a machine or a piece of apparatus. The representative or the salesman can thus visit his patrons and demonstrate very easily the utilization of what he has to sell.

Professor Moureu a Delegate to Washington

In one of my preceding letters I expressed the idea that chemists ought to share in the conference at Washington. The French government, after some hesitation, has adopted this view and by the time these lines appear, Professor Moureu, member of the Institute and professor of the Collège de France, where he succeeded our great Berthelot, will be among you. The welcome which you accorded to Madame Curie makes us sure of the warmth of Mr. Moureu's reception.

The work of Professor Moureu on acetylene compounds and on the rare gases is universally known. At a time when the atomic theory was not yet adopted by all chemists, he was one of the defendants of the new faith and one of his first works was his book on "Notions fondamentales de chimie organique" from which all French chemists have learned organic chemistry. This book is already in its seventh edition in France. It has been translated in all the Latin countries; an English edition, prefaced by Sir William Pope, has just appeared. It is certainly one of the most justly celebrated of the numerous books by Mr. Moureu. I may add that during the war Mr. Moureu was president of the committee of French scientists which directed our Chemical Warfare Service. The services which he rendered in this capacity made him the natural choice for the great mission which is entrusted to him.

A New Petroleum Well

At different times I have called your attention to researches on petroleum which are made at different places in France. A boring in the region of Bugey (department of Ain) has just given a considerable flow, which has lasted for several days. The volume of hydrocarbon gas in twenty-four hours is 100,000 cubic meters.

November 1, 1921

INDUSTRIAL NOTES

The waterworks, at Hopewell, Virginia, which during the war supplied the munitions plant of E. I. duPont de Nemours & Co., as well as adjacent villages, has been sold to the Industrial Service Corporation of Virginia which took over operation of the plant on November 1. The transfer includes electric and steam pumping stations, filtration plant, boiler plant, transmission lines, etc., the plant having a capacity of approximately 30,000,000 gal. per day.

The Universidad Nacional, Tacuba, Mexico, is installing modern equipment to be used in connection with studies in the technology and manufacture of glass.

With the completion of the dyeing plant at Greenville, S. C., a branch of the Franklin Process Co., of Providence, R. I., Greenville will have the last phase necessary to make complete a cycle in cotton manufacturing from raw to finished state. A new process will be employed in that the yarn will be dyed in the wound form instead of the skein, which has been found to be cheaper and more thorough. This will be the only plant of its kind in the South.

The Director of Sales, War Department, has announced that army surplus material costing the United States Government $209,620,147 has been transferred to other governmental departments and establishments. The Department of Agriculture received $138,290,529 worth of the material, nearly 66 per cent, and all but $10,619 of its share was transferred without funds. Acids, chemicals, etc., constituted $19,156,517 worth of the material transferred.

Representative pottery interests at Trenton, N. J., and vicinity are formulating plans to bring about an early readjustment and lowering of freight rates on commodities entering into the manufacture of sanitary pottery, including clay, feldspar, flint, etc. A committee has been appointed to compile data and carry out the details of the movement, under the chairmanship of M. D. Warren, traffic manager of the Chamber of Commerce of Trenton.

Canadian Dyes, Ltd., of Trenton, Ontario, on September 19, 1921, turned out the first batch of dyes ever manufactured in Canada, when about 1700 lbs. of Canadian Direct Blue 2B were successfully finished in the first process of making.

Standardization of the different kinds, qualities, and sizes of window and plate glass was discussed at a recent conference between glass distributors, architects, and engineers of the Bureau of Standards. The conference outlined a program that will be participated in by the manufacturers, distributors, architects, and the Bureau of Standards, and which it is believed will result in the elimination of unnecessary sizes, standardize quality, and enable a more efficient use of this material. Nomenclature in the glass industry will be studied and an effort will be made to define trade terms that are likely to be used with various meanings.

Arrangements are being made for the sale of approximately 81,000 tons of sodium nitrate from the army reserve supply, which has been recommended by officials of the Ordnance Department. The nitrate has been declared surplus and its sale is considered in the interests of the Government as it is at present stored at considerable expense in privately owned warehouses and the army is not in a position to move the 81,000 tons from the private storage into its own storehouse in which the bulk of the nitrate reserve of 300,000 tons is kept. It is expected that the Director of Sales will soon issue a statement calling for sealed proposals on all or any part, which will probably be sold f. o. b. cars.

The Synthetic Ammonia and Nitrates Co., Ltd., a new organization formed under the auspices of Brunner, Mond & Co. Ltd., of England, has commenced the laying out of new works near Middlesbrough. The plant when completed will be used for the manufacture of ammonia, nitrates, and various chemicals.

The Raymond Bros. Impact Pulverizer Company has located its permanent eastern office at 50 Church St., New York City, in charge of Mr. S. B. Kanowitz.

PERSONAL NOTES

Mr. A. P. Gloeckler has resigned as chief chemist of the Tropical Paint and Oil Co., Cleveland, Ohio, and has accepted the position of superintendent of the paint department of the Acorn Refining Co., Cleveland, Ohio.

Mr. Philip L. Gile, formerly connected with the American Agricultural Chemical Co., in their agricultural service bureau, and for eleven years prior to that position chemist of the Porto Rico Agricultural Experiment Station, is at present in charge of the division of soil chemical investigations of the Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

Mr. Alfred S. Halland has resigned as chief chemist of the National Aniline & Chemical Co., Buffalo, N. Y.

Dr. R. L. Sebastian, who was formerly connected with the Department of Health, State of Pennsylvania, in connection with work on mine drainage investigations, has joined the chemical staff of Edgewood Arsenal, Edgewood, Md.

Mr. Herbert Brunt has left the firm of Brunt Dye & Chemical Co., Manchester, England, owned by his father, and has taken over an analytical practice, established in 1870, in London. The name of the firm has been, and will continue to be, Halse and Marshall.

Mr. Thomas J. Keenan recently announced his resignation as Secretary-Treasurer of the Technical Association of the Pulp and Paper Industry in order to accept the position of editor of *Paper*, in the reorganization of which he becomes an officer and stockholder.

Mr. Noah D. Lambert, formerly assistant superintendent of the N. Y. Mutual Gas Light Co., has resigned his position and is now chief engineer and secretary of the Lambert Meter Company, Inc., of Brooklyn, N. Y.

Prof. Sidney S. Negus has recently resigned as head of the chemistry department of the Mercersburg Academy, Mercersburg, Pa., to take up graduate work for his doctorate at the Johns Hopkins University.

Mr. Edward A. Dieterle, assistant chief chemist of the Koppers Co., Mellon Institute, Pittsburgh, Pa., has been made chief chemist of the Chicago By-Product Coke Co., Chicago, Ill.

Mr. Arthur Gallun, of Milwaukee, Wis., and a member of the SOCIETY for a number of years, recently died after an attack of pneumonia. Mr. Gallun was one of the most active organizers of the Leather Division of the A. C. S., and had financed the leather chemistry research at Columbia.

Dr. Clifford S. Leonard, for the past year fellow in chemistry to Sweden on the American-Scandinavian Foundation, has completed his research at the Karoline and Nobel Institutes of Stockholm and has accepted the position of research instructor of pharmacology at the University of Wisconsin.

Mr. H. S. McAree, formerly with the Atlas Powder Co., Landing, N. J., is now engaged in the real estate and insurance business as a member of the firm of Campbell-McAree & Co., Scranton, Pa.

Mr. Leslie R. Olsen, for two years chemist and supervisor of baking operations for the Seattle Baking Co., of Seattle, Washington, has become chief chemist in charge of the laboratories of the International Milling Co., New Prague, Minn.

Mr. L. I. Shaw, assistant chief chemist and assistant chief of the Division of Mineral Technology of the Bureau of Mines, at Washington, D. C., was recently transferred to the Ceramic Station of the Bureau of Mines at Columbus, Ohio, where he is assistant superintendent and in charge of the physico-chemical work.

Mr. A. D. Camp who was formerly with the American Eveready Works, Long Island City, N. Y., has joined the Williamsport Building Products Co., Williamsport, Pa., as factory manager and development chemist.

Mr. Robert Calvert, who was director of the du Pont Company's research laboratory at Arlington, N. J., is now teaching chemistry in the University of Southern California, Los Angeles, Cal., and is also carrying on a general consulting practice.

Mr. Robert G. Dort has severed his connection with the Bregeat Corporation of America, where he was assistant to the vice president, and has become a vice president of the Allied Explorations, Inc., New York City.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

PUBLIC HEALTH SERVICE

Keeping Qualities of Neoarsphenamine in Ampule. G. B. Roth. Public Health Reports, **36** (October 14, 1921), 2523–39. Tables are given to show that market samples of neoarsphenamine may deteriorate in ampule under ordinary conditions. They may change in color, solubility, toxicity, mobility in ampule, and odor after varying periods. The conclusion is reached that commercial neoarsphenamine is a relatively unstable substance in ampule. The results of the experiments suggest (1) that in order to secure further data on its keeping properties, the date of manufacture might be given on the label of all lots issued; (2) that neoarsphenamine should be kept at ice-box temperature.

Comparative Toxicity of Thymol and Carvacrol (Isothymol). A. E. Livingston. Reprint 666 from Public Health Reports. 8 pp. Paper, 5 cents. 1921.

Portable Cyanide Gas Generator for Fumigating Small Compartments. C. M. Fauntleroy. Reprint 673 from Public Health Reports. 8 pp. Paper, 5 cents. 1921.

Direct Inoculation Test for B. Botulinus Toxin, Determination of Presence of B. Botulinus Toxin by Intraperitoneal Inoculation of Laboratory Animals with Suspected Foods. I. A. Bengston. Reprint 677 from Public Health Reports. 8 pp. Paper, 5 cents. 1921.

Death Erroneously Attributed to Chlorinated Water. The Pennsylvania Department of Health, on Post Mortem, Finds That Chlorinated Water Was Not the Cause of Death. From a Report by C. A. Emerson, Jr., Chief Engineer, Pennsylvania Department of Health. Public Health Reports, **36** (October 28, 1921), 2678–9. The conclusion is reached that there is not the slightest evidence that the disinfection of the public water supply had anything to do with the death in question and there is no reason to fear that the chemical disinfection of public water supplies is other than an important safeguard and protection to public health.

Digest of Comments on Pharmacopeia of United States of America. 9th Decennial Revision, National Formulary, 4th Edition, Calendar Year 1918. A. G. DuMez. Bulletin 127. 356 pp. Paper, 25 cents. 1921.

U. S. GEOLOGICAL SURVEY

Lead in 1919. General Report. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1919, Part I. 18 pp. Published October 6, 1921.

The following tabular statement gives the general items regarding domestic production and consumption of refined lead in short tons, for 1918–19.

Production	1918	1919
Domestic desilverized lead	282,024	208,751
Domestic soft lead	210,463	147,744
Domestic desilverized soft lead	47,418	67,938
Total	539,905	424,433
Foreign desilverized lead	100,290	57,787
Total primary[1] lead	640,195	482,220
Antimonial lead	18,570	13,874
Secondary[1] lead	97,100	122,100
Consumption		
Apparent consumption of primary lead, stocks disregarded	542,975	434,143

[1] "Primary lead," which is produced directly from ore, is here distinguished from "secondary lead," which is obtained by refining skimmings, drosses, and old metals. The statistics of secondary lead are given on p. 320. Wherever in this report the word "lead" is used without qualification it means primary lead.

Potash in 1920. M. R. Nourse. Separate from Mineral Resources of the United States, 1920, Part II. 25 pp. Published October 4, 1921.

At the beginning of 1920 the fear of large imports of foreign potash salts still harassed the domestic potash industry, still most of the 66 plants reporting production remained in operation through the year. A few plants reported operation for only the first three months of the year.

About 225,000 short tons of potash (K_2O) were imported in 1920. This, with the 48,077 short tons of domestic output, made the available quantity about equal to that normally used in each of the five years immediately preceding the world war. Because of the low prices received for their produce many of the farmers of the country were unable to take up the promissory notes given by them for fertilizer in the spring of 1920 and were also unable to buy the fertilizer they required in the fall. This condition, coupled with the abundance of potash on the market, resulted in a cancellation by the fertilizer manufacturing companies of orders for domestic potash and greatly reduced the prices of all potash fertilizer materials. As a consequence, all the Nebraska plants were closed by the end of December.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1919. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1919, Part I. 6 pp. Published October 5, 1921. The total value of the gold, silver, and lead produced at mines in South Dakota in 1919 showed a decrease of 26 per cent as compared with the value of metals produced in 1918. The output of gold represented more than 97 per cent of the total value. There were only four producing deep mines in Wyoming in 1919, a decrease of eight mines as compared with 1918.

Antimony in 1920. F. C. Schrader. Separate from Mineral Resources of the United States, 1920, Part I. 12 pp. Published October 27, 1921. The United States in 1915–1918 produced 10,750 short tons of antimony ore, containing 4,310 tons of metal. There has been no production of ore since 1918.

DEPARTMENT OF AGRICULTURE

Composition of Cottonseed. C. F. Creswell and G. L. Bidwell. Department Bulletin 948. 221 pp. Paper, 25 cents. Published September 10, 1921. This bulletin is issued for the guidance of producers, dealers, and crushers in order that they may know more nearly the content of the product in which they are dealing and be better able to judge the value and consequently the price that can be paid for seed. It sets forth data showing as nearly as possible approximate oil and meal yields in each county of the cotton belt.

Drug Plants under Cultivation. W. W. Stockberger. Farmers' Bulletin 666. (Reprint.) 50 pp. Paper, 10 cents.

Pine-Oil and Pine-Distillate Product Emulsions: Method of Production, Chemical Properties, and Disinfectant Action. L. P. Shippen and E. L. Griffin. Department Bulletin 989. 16 pp. Issued October 7, 1921.

Standard and Tentative Methods of Sampling and Testing Highway Materials. Recommended by the Second Conference of State Highway Testing Engineers and Chemists, Washington, D. C., February 23 to 27, 1920. Department Bulletin 949. 98 pp. Paper, 25 cents. Issued October 10, 1921.

The Composition of California Lemons. E. M. Chace, C. P. Wilson, and C. G. Church. Department Bulletin No. 993. 18 pp. Paper, 5 cents. Issued October 15, 1921. A few well-defined differences between the varieties of lemons examined exist, the most striking of which is in the specific gravity of the fruit. The Villa Francas have more oil than the Eurekas. Otherwise no absolute difference in the oil content is shown. A marked difference in sugar content between Eureka and Lisbon lemons exists. There is no difference in the acid content of the three varieties. No correlation is shown between color and thickness of the peel.

Phosphorus in Fertilizer. W. H. Waggaman. Separate 840 from the Yearbook of the Department of Agriculture, 1920. 7 pp. Paper, 5 cents.

Articles from Journal of Agricultural Research

Effect of Ammonium Sulfate upon Plants in Nutrient Solutions Supplied with Ferric Phosphate and Ferrous Sulfate as Sources of Iron. L. H. Jones and J. W. Shive. **21** (August 15, 1921), 701–28.

Bacteriological and Chemical Studies of Different Kinds of Silage. C. A. Hunter. **21** (August 15, 1921), 767–89.

Sandy Crystals in Ice Cream: Their Separation and Identification. H. P. Zoller and O. E. Williams. **21** (August 15, 1921), 791–6.

Reliability of the Nail Test for Predicting the Chemical Composition of Green Sweetcorn. C. O. Appleman. **21** (September 1, 1921), 817–20.

Occurrence of Quercetin in Emerson's Brown-Husked Type of Maize. C. E. SANDO AND H. H. BARTLETT. **22** (October 1, 1921), 1–4.

Microscopic Study of Bacteria in Cheese. G. J. HUCKER. **22** (October 8, 1921), 93–100.

Further Studies on Relation of Sulfates to Plant Growth and Composition. H. G. MILLER. **22** (October 8, 1921), 101–10.

Hydrocyanic Acid in Sudan Grass. C. O. SWANSON. **22** (October 15, 1921), 125–38.

Absorption of Copper from the Soil by Potato Plants. F. C. COOK. **22** (October 29, 1921), 281–7.

COMMERCE REPORTS

The Brazilian market for **chemicals, iron** and **steel,** and **electrical goods** shows improvement. (P. 261)

A distinctly optimistic feeling has arisen in the Chilean situation, due to the belief that the visit of a representative of the nitrogen pool to America will improve the **nitrate** situation. The belief is also growing that competition in artificial fertilizers has been overestimated. The economic condition appears to be better although increased consumption of nitrates by Europe and the United States must precede a definite trade revival. (P. 261)

Attention is directed to recent British developments in **stainless iron** and it is pointed out that this substance is of equal importance with stainless steel. (P. 264)

A report on the Northern Argentine **petroleum fields** is given. Figures are included showing the results of chemical analyses of oils from different localities and a complete record of the test is on file in the Bureau of Foreign and Domestic Commerce. (Pp. 276–8)

According to a decree of the Ministry of Industry and Commerce of Poland dark **crude oil** and similar products may not be exported from Poland without a license. (P. 303)

The production of **petroleum** at the Comodoro Rivadavia fields, from the wells operated by the Argentine government, was 1,936,588 bbls. during the fiscal year, and the production of other wells during the same period is estimated at 230,000 bbls., making a total of 2,266,588 bbls. (P. 314)

Copies of the Bolivian **mineral oil** concession law of June 16, 1921, are now available and may be obtained from the Bureau of Foreign and Domestic Commerce or its district and coöperative offices. (P. 315)

It is reported that the Anglo-Persian Oil Co., under the auspices of the Australian Commonwealth government, is about to prospect for **oil** in Papua, New Guinea. (P. 317)

A report on **"Alcohol Motor Spirit** and Possibilities of Its Production in British Guiana" may be consulted in the Bureau of Foreign and Domestic Commerce or at its district offices. (P. 337)

The Imperial Mineral Resources Bureau has submitted a valuable report on **fluorspar** (fluorite). (P. 341)

The production of **cellulose** in Finland is reviewed. At the end of last July the production of cellulose in Finland was being carried on with practically full force, all of the twenty-four cellulose-producing mills in the country running full time with an approximate yearly output of 300,000 tons of sulfate and sulfite. It is estimated that the total production for the year 1921 will amount to approximately 250,000 tons. (P. 345)

The **drug** and **chemical** market of Argentina is reviewed, and the opinion is expressed that under the present prices of these products from the United States the American manufacturer will possibly lose the market within a short time, the average difference in price between American and European drugs ranging from 40 to 60 per cent. The United States holds a strong position in the industrial trade in Argentina and with favorable prices there should be no difficulty in holding a large share of this trade. (Pp. 352–3)

The production of German **potash** salts has risen very rapidly from less than 8,000,000 tons in 1919 to over 11,000,000 tons in 1920, as is evidenced by the following tabular statement. (P. 353)

1911	9,706,507	1916	8,642,887
1912	11,070,014	1917	8,938,738
1913	11,607,511	1918	9,438,251
1914	8,171,512	1919	7,772,036
1915	6,879,476	1920	11,386,439

The British trade in **linseed** is reviewed. (P. 366)

The Imperial Mineral Resources Bureau has recently issued in its series of monographs, a report respecting **tungsten** ores and concentrates. A tabulated statement is given showing the world's production of tungsten ores from 1913 to 1919. It is pointed out that wolfram concentrates are sold on the basis of 65 per cent tungstic oxide in the British Empire and 60 per cent in the United States. (Pp. 394–5)

Quotations are given from a recent issue of the Japanese-American Commercial Weekly in which the oil policy to be adopted by Japan is briefly outlined. Among other things it was proposed to establish a bureau to carry out investigations. (P. 407)

The construction of **fuel-oil** stations in the Azores is reported. (P. 408)

The United Kingdom has ordered that a customs **duty** of $33^1/_3$ per cent ad valorem shall be paid on the following **imported goods:** laboratory porcelain, compounds (not including ores or minerals) of thorium, cerium, and the other rare earth metals; synthetic organic chemicals (other than synthetic organic dyestuffs, colors, and coloring matters imported for use as such and organic intermediate products imported for their manufacture), analytical reagents, all other fine chemicals (except sulfate of quinine of vegetable origin) and chemicals manufactured by fermentation process. (P. 418)

Czechoslovakia has suspended the import duties on **zinc** ash, zinc slag, and dross. (P. 418)

Italy has authorized the free admission of colored **paper pulp.** (P. 418)

Portugal has abolished export surtaxes on **carbon sulfide.** (P. 418)

Kaolin is now subject to a Portuguese surtax, but all minerals except **tin** and tin ore may now be exported without payment of an export surtax. (P. 419)

A reduction has been made in Rumanian export duties on light **benzene,** heavy benzene, lamp oil, light **oils** and heavy oils. (P. 419)

The French export prohibition on illuminating **oils** has been removed. (P. 419)

The **dyestuffs** sent to Japan as war compensation from Germany will again be sold in public tender, the first tender being deemed too low by the government. It is generally believed, however, that the second tender will only bring forth still lower offers as the dye market is daily becoming worse. (P. 425)

The production of **iron** ore in France during the first six months of 1921 was 7,532,868 tons—1,693,464 tons more than the output in the first half of 1920. (P. 453)

The **petroleum** industry in Mexico is reviewed in considerable detail. In 1913 Mexico furnished but one-fifteenth of the world's supply of oil; in 1920 it furnished nearly one-fourth. A comparison of the following figures of oil produced in Mexico, in the United States and in the world since 1901, indicates the phenomenal growth of this industry in Mexico. (Pp. 463–8)

Years	Mexico Bbls.	United States Bbls.	Total World Production Bbls
1901	10,345	69,620,529	167,434,434
1902	40,200	88,766,916	182,006,076
1903	75,375	100,461,337	194,879,669
1904	125,625	117,080,960	218,204,391
1905	251,250	134,717,580	215,292,167
1906	502,500	126,493,936	213,415,360
1907	1,005,000	166,095,335	264,245,419
1908	3,932,900	178,527,355	285,552,746
1909	2,713,500	183,170,874	298,616,405
1910	3,634,080	209,557,248	327,937,629
1911	12,552,798	220,449,391	344,174,355
1912	16,558,215	222,935,044	352,446,598
1913	25,696,291	248,446,230	383,547,399
1914	26,235,403	265,762,535	403,745,342
1915	32,910,508	281,104,104	427,740,129
1916	40,545,712	300,767,158	461,493,226
1917	55,292,770	335,315,601	506,702,902
1918	63,828,326	355,927,716	514,729,354
1919	87,072,955	377,719,000	544,885,000
1920	163,540,000	443,402,000	688,474,251[1]
1921 (first 6 months)	98,827,665	236,675,000[1]	.....

[1] Estimated.

A final and interesting report has been issued by the Department of Scientific and Industrial Research in regard to **nitrogen** products in which it is observed that no definite conclusions are yet possible as to the post-war demand for fixed nitrogen, and especially that required for fertilizing purposes. (P. 469)

The resin, turpentine, pitch, and **naval stores** industry in Spain is controlled by La Union Resinera Espanola, which has recently made an alliance with the German firm for the purpose of enlarging its activities. The new company will engage in the manufacture of products derived from the distillation and refining of resin, and fish and olive oils. It will make varnishes, enamels, prepared driers, paints, linoleum, glue, aniline and other chemicals, including synthetic camphor. (P. 470)

Statistics are given showing the production and sales of **resinous products** in Spain for the years 1915–19. (P. 470)

The production of **resin** and similar products in Portugal for the years 1916–1921 is shown. (P. 471)

On the Tyne the Walbottle Coal and Fireclay Co., Ltd. has decided to change from the production of **coal** to the making of coal by-products. (P. 472)

A recent French decree increases the **import tariff** by fixing coefficients on the following articles: liquid chlorine, ordinary hydrochloric acid, liquid sulfurous acid, sulfate of aluminium, alum of ammonium and of potassium, peroxide of barium, and chloride of magnesium. (P. 477)

The restriction of the exportation of **bauxite**, together with the 20 per cent ad valorem duty, has been removed. (P. 478)

An Italian decree extends until December 31, 1921, the period during which **saccharin**, and the raw materials from which it is made, may be placed on sale in Italy. (P. 479)

The mineral resources of the Balkan and Near Eastern Countries are described, particular attention being directed to the **minerals** of Anatolia and the production of **petroleum** in Egypt. (Pp. 488–9)

The **petroleum** industry in Mexico is reviewed in an article which deals with the laws affecting the development of Mexican oil fields, court decisions, and regulations governing oil exploitation in Mexico. (Pp. 515–9)

The situation of the **oil** companies in Rumania is more satisfactory at present than it has been since the war. (P. 519)

Negotiations concerning the Polish **oil** resources are to be renewed. (P. 519)

A very promising but undeveloped **oil** field is thought to exist in the extreme north of Siam. Seepages have been found and it is understood that some shallow borings have yielded petroleum of a good quality with an asphalt base. (P. 519)

The British supply of **antimony** is described. (Pp. 526–7)

A new German process has been devised to utilize **rice waste.** The process is reported to be a simple chemical reaction whereby cellulose, coke filter material and paraffin, phenolin, carbonic-acid gas, carbon monoxide, hydrogen, and acetic acid are obtained in sufficient quantities to be of commercial use. (P. 550)

STATISTICS OF EXPORTS TO THE UNITED STATES

EUROPE—(P. 263)
Pig iron
Tin plate

GREECE—(P. 306)
Tanning extracts
Tanning materials
Olive oil, edible
Olive oil for mechanical uses

BELGIUM—(P. 524)
Varnish, nonalcoholic
Paints and dyes except logwood

PALESTINE AND SYRIA—(P. 306)
Olive oil, edible

NORWAY—(P. 345)
Wood pulp, chemical
Wood pulp, mechanical

LONDON, ENGLAND—(P. 365)
Tin
Drugs and chemicals
Leather
Hides
Gums

SOUTH AFRICA—(P. 378)
Concentrates:
  Lead and copper
  Vanadium
Copper, excluding matte
Copper matte
Copra
Corundum, crystalline
Hides, cattle:
  Dry
  Wet, salt
Ore:
  Copper
  Chrome
  Corundum, excluding crystals
  Corundum, crystals
  Manganese
  Vanadium
Wax

SWITZERLAND—(P. 498)
Aniline dyes

BOOK REVIEWS

Estate Rubber—Its Preparation, Properties, and Testing. By O. DE VRIES. xi + 649 pp. Drukeryen Ruygrok & Co., Batavia, 1920. Price, 20 fl. (about $6.50).

It is extremely difficult to outline adequately, within the limits of a review, the contents of the above volume. The book is not, as it makes no pretense to be, a treatise on our present scientific knowledge regarding the preparation and properties of raw rubber, but it is rather a vade-mecum for the up-to-date rubber estate manager or chemist, from which both are left to draw their own conclusions. The book is written largely from the results of researches carried out by the author or under his direction at the Institute, Buitenzorg, Java. Contemporary literature has been carefully cited and extracted, and but for the fact that much of the earlier scientific literature is unmentioned, the volume might be considered as a most valuable work for reference purposes.

In the opening chapters the composition and properties of the latex are described in great detail, and the influence of coagulants, anticoagulants, antiseptics and other chemicals, and methods of treatment of the latex on the composition and properties of the raw rubber and serum are discussed. One chapter is devoted entirely to a comparison of smoked sheet rubber with first latex crepe, based on physical and chemical tests made by the author and others. That the actual difference between these two well-known grades of commercial rubber is as insignificant as the author would have us believe will be hard to convince American rubber manufacturers. There are chapters on the keeping qualities of rubber, forms of deterioration and defects in raw rubber, and on special methods of preparation of rubber, including a comparison of the Brazilian method.

The succeeding chapters deal with the vulcanization of raw rubber and with the methods employed by the Institute of Buitenzorg for the evaluation of samples of rubber, raw or vulcanized. The reason for leaving the treatment of this subject for the latter part of the book is not obvious, particularly as methods of testing are referred to, time and again, in the earlier chapters. A complete and detailed account of the method of mixing, vulcanizing and physical testing employed by the Institute and used in connection with the preparation of the curves and data sheets employed in the book, is given. In our opinion the physical tests are insufficient really to differentiate the inner properties of different rubbers from a manufacturing standpoint, or to bring out the extent of these differences.

The final chapter is devoted to the chemical composition of raw rubber and to the judging of raw rubber on the exterior. The book is so replete with data and curves bearing on the various factors influencing the preparation and properties of raw rubber that it should be read with interest by estate managers and rubber chemists alike.

D. SPENCE

Technical Records of Explosives Supply, 1915-1918. I. Denitration of Spent Acids. 56 pp., 25 illustrations. 12s. 6d. **II. Manufacture of Trinitrotoluene (TNT).** 116 pp., 63 illustrations. 17s. 6d. Ministry of Munitions and Department of Scientific and Industrial Research, London, H. M. Stationery Office, 1920. 19 x 28 cm. each.

These are the first two of a special series of reports designed to make results of technical and scientific value gained in the development and operation of the National Factories during the war available to the industries concerned. As all the factories of the country were under governmental supervision and control there was an unparalleled opportunity to secure accurate data on a large scale which was insured by the plan of chemical control instituted by Mr. Kenneth B. Quinan, and these publications represent an endeavor to retrieve some of the enormous wastage of war.

The titles of these books well indicate the nature of their contents, but though, in Volume I, it is pointed out that guncotton spent acids are denitrated in "stills," and those from TNT and nitroglycerin by steam in columns or "denitrators," only the latter method is dealt with in detail, emphasis being laid particularly on TNT acids. Likewise, regarding the nitration of toluene, while the several step by step and the single stage processes are each considered, for purposes of detailed description the plant at Queen's Ferry is taken, as it was the largest, erected on a very extensive scale, and embodied the results of a very wide engineering knowledge of chemical plants. At Oldbury a continuous process plant was erected with a rated capacity of 100 tons per week which proved capable of producing some 500 tons per week, starting with MNT from Borneo spirit.

The figures consist largely of folded plates (some 110 by 52 cm. in area) giving plans, to scale, of the apparatus, or of diagrams, such as that of the "ultimate destination of nitrogen in TNT manufacture," which enable one to apply the most precise checks at all points. In addition there are diagrammatic schemes of operation which state the masses, temperatures, and times involved with such definiteness it would be difficult to fail in manufacture if they were followed. Moreover copies of blank forms such as "TNT Washers—Sulfite Purification" for factory use add to the assurance of success.

This series of reports is prepared by Mr. W. Macnab and they are presented in excellent form for use, being printed in fourteen point, clear faced type, on heavy calendered paper, while the text is remarkably free from typographical errors, and the dimensions make the books quite convenient for use. The only suggestion to be made which would render the valuable contents of these admirable volumes more easily accessible is the addition of indexes, and a more liberal use of titles on the plates.

Everyone engaged in the production of sulfuric, nitric, and mixed acids, in the recovery of spent acids, or in conducting nitration processes, will need these books, while no student of chemical engineering should be permitted to graduate until he has become acquainted with their contents and worked out problems based on the information they convey.

CHARLES E. MUNROE

A French-English Dictionary for Chemists. BY AUSTIN M. PATTERSON. xvii + 384 pp. John Wiley & Sons, Inc., New York, 1921. Price, $3.00, postpaid (18s. net).

The importance of French chemical industry was brought home to most American chemists by the magnificent effort made by French chemists during the war. We are all familiar, of course, with the achievements of the French scientific chemistry as differentiated from the applied side of our science, but the increasing importance of the latter has made it necessary for technical chemists to consult French publications more and more, and the need of a compact dictionary giving particular attention to technical meanings and interpretations has been increasingly felt. That need is admirably provided for in the volume under consideration.

"A really good dictionary is a growth," truly says the author in the preface, and naturally one cannot expect a first edition to be free from imperfections. There are several matters that will need attention in a subsequent edition.

The geographical nomenclature leaves much to be desired. There are some very important omissions and many inconsistencies. Peru, Bolivia, and Brazil are given, but neither Chile nor the Argentine Republic. The spelling in English and French is very similar in all of these and if one is given the others should be given also. A more serious omission occurs in the translation of the French word *argentin*, which is given only as "silvery," whereas it means also pertaining to or coming from the Argentine Republic. The French Departments and cities should receive more extended attention. Auvergne is not mentioned at all and the adjective *auvergnat*, meaning coming from Auvergne, is translated only in its technical meaning of "tanning liquor." This might prove to be puzzling to those unfamiliar with French geography. Of our own states California is given but not Louisiana, although the difference in the French and English spelling is the same in both cases. Havre and Havana are never spoken of singly in French but always accompanied by the article, *Le Havre*, *La Havane*, just as we always say "The Hague" and not merely "Hague." Many other additions of geographical names and especially adjectives would be valuable.

The objection might be made that the above suggestions might interfere with the compactness of the Dictionary, but in many other respects it could be cut down so as to make more than the necessary room for the geographical terms that are likely to be met in technical literature. Is it necessary to translate under *alcool* a long list of rather rare alcohols, such as myricyl alcohol, octyl alcohol, piperonyl alcohol, etc.? No serious hardship would entail to the chemical profession by having those of its members who work with these compounds look up the meaning of *caprylique*, *myricique*, *piperonilique* under the letters "C," "M," and "P" instead of having them thus doubly classified. Under *bleu* there is also a long list such as Berlin blue, Nicholson's blue, Prussian blue, etc., which could be safely omitted. Lives there a chemist with soul so dead that on finding that the French word *acide* means "acid" he must needs have a special reference to tell him that *acide-H* means H-acid and *acide-G* means G-acid?

The French evolved during the war an extensive nomenclature, supposedly a secret code, for the designation of war gases. The secrecy, however, proved to be more apparent than real, as captured documents proved later and although the names were mostly abandoned towards the end of the war, they are to be found in much of the French literature on war gases (*Chimie et Industrie*, **2**, 1377). It might be helpful to the future chemists engaged in research in chemical warfare to have some of the more common ones included in the dictionary. "Yperite" was the only one noticed.

The feminine gender has been the cause of several slips which should be corrected in the next edition. The adjectives of *Burette anglais*, *Boisson fermenté*, *Chaine anglais*, *Eau sedatif*, *Eau thermal*, *Etoupille fulminant*, *Etuve esterilizateur*, *Herbe empoisonné*, *Huile litharge*, *Huile lythargyré*, *Masse demi-affiné*, *Poudre brisant* should be changed to the feminine. Those of *Flacon marine*, *Procedé marseillaise*, *Carton minerale* should be changed to the masculine. *Atelier de teinture* should be changed to *Atelier de peinture* if it is to mean a painter's studio. *Acier nickelé* should be translated as "nickel plated steel" as well as "nickel steel" as both meanings are common, especially the former, which was omitted. *Artifice d'éclairant* should be *artifice éclairant* as *éclairant* is an adjective and not a noun. *Avocatier* is not an alligator pear but the tree bearing alligator pears. *Blanc de Holland* should be *Blanc de Hollande*.

In the chemical nomenclature there are a few omissions. Butalanine is given, but neither butane nor hexane. *Etain gris* is translated as "bismuth," an antiquated appellation going back to the alchemists, whereas the more important translation of "gray tin" is omitted. These, however, are few and not very important.

Some translations might be objected to. *Arme blanche* is translated as "side arm." This is not correct. It means a cutting, or piercing, steel weapon. A revolver is a side arm but not an *arme blanche*, and a spear is an *arme blanche* but not a side arm.

The English proofreading has been excellent, only one misprint coming to the reviewer's attention: namely, "nickel plating" on page 240 which is misspelled "nickle plating."

But after all, these are only minor criticisms. The author has done an excellent piece of work in bringing together in a very compact form a vast number of technical words and phrases, the meanings of which would be difficult to find even in the largest dictionaries, except at the cost of much labor. With the increasing importance of French technical publications this dictionary should be found in every chemical library, public or private, in the university as well as in the technical laboratory.

The printing, paper, and the flexible binding are of the best and the book is highly recommendable as a useful purchase.

J. ENRIQUE ZANETTI

NEW PUBLICATIONS

Aluminium and Its Alloys. C. Grard. 184 pp. Constable & Co., Ltd., London.

Animal Proteins. Hugh Garner Bennett. (Industrial Chemistry Series.) 287 pp. Price, $3.75. D. Van Nostrand Co., New York.

Benzine and Mineral Lubricants, Their Production, Testing and Uses. Translated from the German of J. Formanek. Revised 256 pp. Illustrated. Price, 15s. net. Scott, Greenwood & Son, London

Bleaching: Being a Resumé of the Important Researches on the Industry Published during the Years 1908–1920. S. H. Higgins. (Economic Series.) 137 pp. Price, $3.75. Longmans, Green & Co., New York.

Chemical Disinfection and Sterilization. S. Rideal and E. K. Rideal. 313 pp. Price, 21s. Arnold & Co., London

Chemical Warfare: Riddle of the Rhine: Chemical Strategy in Peace and War. V. Lefebure. 277 pp. Price, 10s. 6d. W. Collins Sons & Co., Ltd., London.

Colloids: The Chemistry of Colloids. W. W. Taylor. 532 pp. Price, 10s. 6d. net. Edward Arnold, London.

Combustibles et Huiles de Graissage pour Moteurs Diesel. W. Schenker. 94 pp. Price, 13fr. Dunod, Paris.

Combustibles Industriels. F. Colomer and Charles Lordier. 4th Edition. 704 pp. Price, 60fr. Dunod, Paris.

Cosmetics. Theodor Koller. 3d Edition. 269 pp. Price, $3.50. D. Van Nostrand Co., New York.

Dictionary: Popular Chemical Dictionary. C. T. Kingzett. 375 pp. Price, $4.00. D. Van Nostrand Co., New York.

Famous Chemists: The Men and Their Work. Sir William Tilden. 296 pp. Price, 12s. 6d. G. Routledge & Sons, London. E. P. Dutton & Co., New York.

Fixation of Atmospheric Nitrogen. John Knox. 121 pp. Price, 4s. net. Gurney & Jackson, London.

Food Chemistry: Méthodes Actuelles d'Expertises Employées au Laboratoire Municipal de Paris et Documents sur les Matières Relatives a l'Alimentation. André Kling. 326 pp. Illustrated. Price, 32fr. net. Dunod, Paris.

Food Products, Source, Chemistry and Use. E. H. S. Bailey. 2d Edition, revised. 550 pp. Price, $3.00. P. Blakiston's Son & Co., Philadelphia.

Handbook of Chemistry and Physics. Charles D. Hodgman, M. F. Coolbaugh and C. E. Senseman. 8th Edition. 711 pp. Price, 24s. Chapman & Hall, Ltd., London.

Industrial Hydrogen. Hugh S. Taylor. A. C. S. Monographs. 200 pp. Price, $3.50. Chemical Catalog Co., Inc., New York.

Inorganic Chemistry: Notes on Inorganic Chemistry. F. Francis. 244 pp. Price, 8s. 6d. net. Simpkin, Marshall, Hamilton, Kent & Co., Ltd., London.

Laboratories: Their Plannings and Fittings. A. E. Munby. 220 pp. Price, 25s. net. G. Bell & Sons, Ltd., London.

Leather Chemistry: Practical Leather Chemistry. Arthur Harvey. 193 pp. Price, $3.75. Crosby, Lockwood & Son, London.

Metallurgy: Traité de Métallurgie Générale. Léon Guillet. 541 pp. Illustrated. Price, 50fr. J.-B. Baillière, Paris.

Microscopy: Critical Microscopy. Alfred C. Coles. 104 pp. Price, 7s. 6d. net. J. & A. Churchill, London.

Modern Chemistry, Pure and Applied. Arthur J. Hale. Vol. I. 272 pp. Vol. II. 276 pp. Price, 16s. net per volume. Virtue & Co., London.

Oil-Field Practice. Dorsey Hager. 310 pp. Illustrated. Price, $3.00. McGraw-Hill Book Co., Inc., New York.

Organic Chemistry: An Introduction to Organic Chemistry. D. L. Hammick. 258 pp. Price, 6s. net. G. Bell & Sons, Ltd., London.

Organic Chemistry: Study Questions in Elementary Organic Chemistry. Alexander Lowy and Thomas B. Downey. 91 pp. Price, $1.00. D. Van Nostrand Co., New York.

Organic Syntheses. Roger Adams, Editor-in-Chief. 84 pp. Illustrated. Price, $1.50. John Wiley & Sons, Inc., New York.

Qualitative Analysis: A Textbook of Qualitative Analysis of Inorganic Substances. Sydney Alexander Key. 80 pp. Price, 7s. 6d. net. Gurney & Jackson, London.

Silver Ores. H. B. Cronshaw. 152 pp. Price, 6s. net. John Murray, London.

Soil Conditions and Plant Growth. E. J. Russell. (The Rothamsted Monographs on Agricultural Science.) 406 pp. Price, $5.00 net. Longmans, Green & Co., New York.

Tanning Materials. Arthur Harvey. 174 pp. Crosby, Lockwood & Son, London.

Waste in Industry. Committee on Elimination of Waste in Industry of the Federated American Engineering Societies. 402 pp. Price $4.00. McGraw-Hill Book Co., Inc., New York.

RECENT JOURNAL ARTICLES

Alcohol: La Fabbricazione Industriale dell' Alcool dalle Carrube. Giuseppe Mezzadroli. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 9, pp. 399–403.

Bearing Metals and Their Industrial Value. Z. Czochralski. *Brass World*, Vol. 17 (1921), No. 9, pp. 245–48. Abstracted from *Zeitschrift für Metallkunde*, 12, 371–403.

Blast Furnace Flue Dust—100% Recovery. George B. Cramp. *The Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 11, pp. 648–53.

Cellulose: La Fabrication de la Cellulose a l'Aide du Chlore. Umberto Pomilio. *Chimie et Industrie*, Vol. 6 (1921), No. 3, pp. 267–75.

Coal: A Resumé of Standard Methods in Sampling, Analysis and Classification of Coal. A. Trevor Williams. *Journal of the Chemical, Metallurgical and Mining Society of South Africa*, Vol. 22 (1921), No. 1, pp. 1–15.

Coal: The Froth Flotation of Coal. Frank Butler Jones. *The Coal Industry*, Vol. 4 (1921), No. 10, pp. 505–09.

Dyes: Fastness of Dyeings to Storing. Oscar R. Flynn. *Textile World*, Vol. 60 (1921), No. 18, pp. 63–4.

Dyes: The Modern Dyestuff Industry. H. E. Fierz. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 19, pp. 364r–66r.

Electroanalyse Rapide. Arnold Lassieur. *Bulletin de la Société Chimique de France*, Vol. 19 (1921), No. 9, pp. 753–80.

Enamels: The Causes and Control of Fish Scaling of Enamels for Sheet Iron and Steel. R. R. Danielson and W. H. Souder. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 8, pp. 620–54.

Glass: The Manufacture of Glass Milk Bottles. A. L. Brown. *The Glass Industry*, Vol. 2 (1921), No. 11, pp. 259–62.

Glass: The Manufacture of Glass with Indigenous Alkali. J. P. Srivastava and D. Sinha. *Journal of Indian Industries and Labour*, Vol. 1 (1921), Part 3, pp. 333–40.

Hydrogen Ion: The Colorimetric Method of Determining Hydrogen-Ion Concentration: Some Applications in the Analytical Laboratory. Norman Evers. *The Analyst*, Vol. 46 (1921), No. 547, pp. 393–99.

Leather: Notes on Water Extraction of Leather. F. P. Veitch and R. W. Frey. *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 9, pp. 491–502.

Leather: The Effect of Atmospheric Humidity on the Determination of Moisture in Leather. F. P. Veitch and T. D. Jarrell. *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 10, pp. 547–58.

Leather: The Removal of Elastin during Bating. Robert H. Marriott. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 8, pp. 280–88.

Leather: Some Applications of Synthetic Tanning Materials. J. B. Hill and G. W. Merryman. *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 9, pp. 484–91.

Leather: Swelling of Hide Powder. Part I. Eric C. Porter. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 8, pp. 259–67.

Paper: Fundamental Chemistry in Paper Making. J. L. A. Macdonald. *Paper*, Vol. 29 (1921), No. 7, pp. 12–17; *Pulp and Paper Magazine of Canada*, Vol. 19 (1921), No. 42, pp. 1067–69.

Paper: Die Verwendung von Warme und Kraft in der Papierindustrie. Fredrik Grewin. *Der Papier-Fabrikant*, Vol. 19 (1921), No. 38, pp. 1025–32.

Rubber: The Acceleration of Vulcanization by Organic Accelerators. A. Maximoff. *The Rubber Age*, Vol. 10 (1921), No. 1, pp. 11–12, 14; *Le Caoutchouc et la Gutta Percha*, 1921, 10944–47.

Salvarsan: Le 606 ou Salvarsan. M. Toussaint. *Chimie et Industrie*, Vol. 6 (1921), No. 3, pp. 296–304.

Steel: Carbonizing in Fused Sodium Carbonate. Walter A. Jayme *Forging and Heat Treating*, Vol. 7 (1921), No. 10, pp. 507–12.

Steel: Forging Experiments with Mild Steels. Paul Junkers. *Forging and Heat Treating*, Vol. 7 (1921), No. 10, pp. 518–24. Translated from *Stahl und Eisen*, 41, 677–78.

Steel: Low Temperature Carbonization and Its Relation to the Iron and Steel Industry. A. Thau. *The Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 11, pp. 645–48.

Sugar: Use of Invertase for Sucrose Estimation. T. Swann Harding. *Sugar*, Vol. 23 (1921), No. 10, pp. 546–48.

Vulcanization Tests on Hexamethylene Tetramine, Formaldehyde Aniline and Aldehyde Ammonia. C. S. Williams. *The India Rubber World*, Vol. 65 (1921), No. 2, pp. 101–06.

Zirconia Cements. Mark Sheppard. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 8, pp. 662–68.

MARKET REPORT—NOVEMBER, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Nov. 1	Nov. 15
Acid, Boric, cryst., bbls	lb.	.12$^3/_4$	.12$^3/_4$
Hydrochloric, com'l, 20°	lb.	.01$^1/_2$	.01$^1/_2$
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07	.07
Phosphoric, 50% tech	lb.	.12	.12
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	17.00	17.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb.	*.03$^1/_2$	*.03$^3/_4$
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	*.07	*.07
Ammonia Water, carboys, 26°	lb.	.08	.08
Arsenic, white	lb.	.06	.06
Barium Chloride	ton	*60.00	*60.00
Nitrate	lb.	*.07$^3/_4$	*.07
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works	100 lbs.	2.25	2.25
Borax, cryst., bbls	lb.	.05$^3/_4$	.05$^3/_4$
Bromine, pure	lb.	.20	.20
Calcium Chloride, fused	ton	28.75	28.75
Chalk, precipitated, light	lb.	.03$^1/_2$	.03$^1/_2$
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.25	5.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.50	3.50
Lead Acetate, white crystals	lb.	.12	.12
Nitrate	lb.	.15	.15
Red American	100 lbs.	.08	.08
White American	100 lbs.	.06$^1/_2$	.06$^1/_2$
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	*1.40	*1.40
Magnesium Carbonate, tech	lb.	.10	.10
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*38.00	*40.00
Phosphorus, yellow	lb.	.30	.30
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.11	.11
Bromide, imported	lb.	*.14	*.15
Carbonate, calc., 80–85%	lb.	.05	.05
Chlorate, cryst	lb.	*.06$^1/_2$	*.06$^1/_2$
Hydroxide, 88–92%	lb.	*.05$^1/_2$	*.05$^1/_2$
Iodide, bulk	lb.	2.60	2.60
Nitrate	lb.	08	.08
Permanganate, U. S. P.	lb.	*.18	*.16
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.48	.45$^1/_2$
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.15	2.15
Caustic, 76%	100 lbs.	4.00	4.00
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.08	.08
Chlorate	lb.	.07$^1/_2$	.07$^1/_2$
Cyanide	lb.	*.27	*.27
Fluoride, technical	lb.	*.10	*.10
Hyposulfite, bbls	100 lbs.	3.50	3.50
Nitrate, 95%	100 lbs.	2.45	2.45
Silicate, 40°	lb.	.01$^1/_2$	.01$^1/_2$
Sulfide 60% fused	lb.	.06	.06
Bisulfite, powdered	lb.	.04$^1/_2$	.04$^1/_2$
Strontium Nitrate	lb.	*.12	*.12
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride	lb.	.18	.18
Oxide	lb.	.40	.40
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.09	.09

ORGANIC CHEMICALS

		Nov. 1	Nov. 15
Acetanilide	lb.	*.29	*.29
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.10	.10
Acetylsalicylic	lb.	.56	.65
Benzoic, U. S. P., ex-toluene	lb.	.65	.65
Carbolic, cryst., U. S. P., drs.	lb.	.09	.10
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	*.45	*.45
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.15	.14
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.20	.22
Tartaric, crystals, U. S. P.	lb.	*.28	*.28
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12$^1/_2$	.12$^1/_2$
Alcohol, denatured, complete	gal.	.40	.40
Ethyl, 190 proof	gal.	4.75	4.75
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap. refined	lb.	.74	.91
Carbon Bisulfide	lb.	.06$^1/_2$	.06$^1/_2$
Tetrachloride	lb.	.10$^1/_2$	.10$^1/_2$
Chloroform, U. S. P.	lb.	*.38	*.38
Creosote, U. S. P.	lb.	.40	.40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.45	2.45
Imported Potato	lb.	.08$^1/_2$	.08$^1/_2$
Ether, U. S. P., conc., 100 lbs.	lb.	.16	.14
Formaldehyde	lb.	*.11	*.10$^1/_2$
Glycerol, dynamite, drums	lb	.12$^1/_2$	.12$^1/_2$
Methanol, pure, bbls	gal.	.85	.85
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	1.88	1.88
Potato, Jap	lb.	.06	.06
Rice	lb.	.18	.18
Sago	lb.	.04	04

OILS, WAXES, ETC.

		Nov. 1	Nov. 15
Beeswax, pure, white	lb.	.37	.37
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10$^1/_2$	.10$^1/_2$
Ceresin, yellow	lb.	.08	.08
Corn Oil, crude, tanks, mills	lb.	.07$^3/_4$	.07$^3/_4$
Cottonseed Oil, crude, f. o. b. mill	lb.	.07	.06$^3/_4$
Linseed Oil, raw (car lots)	gal.	.67	.69
Menhaden Oil, crude (southern)	gal.	.33	.33
Neat's-foot Oil, 20°	gal.	1.00	1.00
Paraffin, 128–130 m. p., ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	6.00	6.00
Rosin Oil, first run	gal.	.35	.35
Shellac, T. N.	lb.	.65	.64
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.75	.75
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.83	.80

METALS

		Nov. 1	Nov. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.85	4.85
Bismuth	lb.	1.55	1.65
Copper, electrolytic	lb.	.13	.13
Lake	lb.	.13	.13
Lead, N. Y.	lb.	.04$^3/_4$	.04$^3/_4$
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	78.00	78.00
Quicksilver, flask	75 lbs. ea.	*38.00	*40.00
Silver, foreign	oz.	.70	.70$^3/_4$
Tin	lb.	.28	.28
Tungsten Wolframite	per unit	3.25	3.25
Zinc, N. Y.	100 lbs.	5.00	5.00

FERTILIZER MATERIALS

		Nov. 1	Nov. 15
Ammonium Sulfate, export	100 lbs.	2.65	2.65
Blood, dried, f. o. b. N. Y.	unit	4.00	4.00
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	3.50 & .10	3.50 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.75	.75
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American maker's price).

COAL-TAR CHEMICALS

Crudes

		Nov. 1	Nov. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	.07	.07
Phenol, drums	lb.	.09	.10
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.45	.45

Intermediates

		Nov. 1	Nov. 15
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.25	2.25
H	lb.	1.10	1.10
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.40	2.40
Naphthionic, crude	lb.	.70	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.27	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.18	18
Aniline Salt	lb.	.26	.26
Anthraquinone	lb.	1.50	1.50
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.40	1.40
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.45	.45
Dinitrobenzene	lb.	.21	.21
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.65
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.15	90
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.12	.12
Monoethylaniline	lb.	2.00	2.00
a-Naphthylamine	lb.	.32	.32
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.32	.32
m-Nitroaniline	lb.	.85	.85
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	.13	.13
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.85	.85
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.70	1.70
Phthalic Anhydride	lb.	.40	.40
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	2.00	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.40	.40
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.45	.45
o-Toluidine	lb.	.25	.25
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Nov. 1	Nov. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50

Acid Colors (*Concluded*)

		Nov. 1	Nov. 15
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.70	.70

Direct Colors

		Nov. 1	Nov. 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Nov. 1	Nov. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Nov. 1	Nov. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		Nov. 1	Nov. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.75	.75
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Nov. 1	Nov. 15
Auramine, O, domestic	lb.	2.25	2.25
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2 00
Malachite Green, crystals	lb.	2.00	2 00
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc	lb.	10 00	10.00
Victoria Blue, base, domestic	lb.	5 40	5.40
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00

AUTHOR INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY
VOLUME XIII—1921

ABRAMS, A. Effect of Chemical Reagents on Microstructure of Wood. (*Correction*, 960) 786
Adolph, W. H. Chemical Industry in China 1099
Alford, E. C. Plate and Frame Filter Presses. Filtration Symposium, New York Meeting, A. C. S. 1000
Alliott, E. A. Washing and Washing Ports in Connection with "Chamber" and "Frame" Filter Presses. Filtration Symposium, New York Meeting, A. C. S. 976
Almy, L. H. and E. Field. Preservation of Fish Frozen in Chilled Brine. I—Penetration of Salt 927
Anderson, R. P. and C. E. Hinckley. Gasoline from Natural Gas. V—Hydrometer for Small Amounts of Gasoline 144
Andrews, A. B. Notes on Laboratory Apparatus 560
Andrews, C. E. History of the Preparation and Properties of Pure Phthalic Anhydride. [*See* This Journal, **12** (1920), 1017] 167
Andrews, H. I. and R. H. Clark. The Tannin Content of Pacific Coast Conifers 1026
Atkins, H. D. The Atkins-Shriver Automatic Filter Press. Filtration Symposium, New York Meeting, A. C. S. 1006
Austin, M. M. with S. W. Parr. Potash Shales of Illinois 1144
Ayres, E. E., Jr. Common Characteristics of Crude Petroleum Emulsions. Emulsification Symposium, New York Meeting, A. C. S. 1010

BAEKELAND, L. H. and M. Harvey. Further Studies on Phenolic Hexamethylenetetramine Compounds 135
Bailey, A. and W. C. Taylor. Graded Seal for Joining Pyrex to Lead Glass 1158
Bailey, C. H. and F. A. Collatz. Activity of Phytase as Determined by the Specific Conductivity of Phytin-Phytase Solutions 317
  Studies of Wheat Flour Grades. I—Electrical Conductivity of Water Extracts 319
  and A. C. Peterson. Studies of Wheat Flour Grades. II—Buffer Action of Water Extracts 916
Bailey, G. C. and F. Boettner. Production of Coumarins from Maleic and Malic Acids 905
Baker, F. P. Study of the Fundamental Laws of Filtration Using Plant-Scale Equipment. (*See* Sperry, 1163) 610, 1163
Bancroft, W. D. Chemistry and Civilization, by Cushman. (Book Review) 494
  Factory Chemistry, by Hawkes. (Book Review) 663
  Research Problems in Colloid Chemistry 83, 153, 260, 346
Barnard, D. P., 4th, and R. E. Wilson. Condensation Temperatures of Gasoline- and Kerosene-Air Mixtures 906
  Total Sensible Heats of Motor Fuels and Their Mixtures with Air 912
Bartow, E. Sewage Testing Station of Illinois State Water Survey Division 945
Baskerville, C. Anniversary Celebration at the Chemists' Club 267
  Margarine, by Clayton. (Book Review) 181
  Report of the A. C. S. Committee on Occupational Diseases in the Chemical Trades 568
  and P. W. Cohen. Solvents for Phosgene 333
  and M. Hirsh. Rate of Evaporation of Ethyl Chloride from Oils 322
  and C. M. Joyce. Regenerating Bookstock 214
  and R. Stevenson. Recovering Newsprint 213
Bateman, E., C. J. Humphrey and R. M. Fleming. Studies on the Toxicity of Wood Preservatives—III 618
Bates, F. J. Report of the Division of Sugar Chemistry. New York Meeting, A. C. S. 957
Bebie, J. Pure Phthalic Anhydride. [*See* Gibbs, This Journal, **12** (1920), 1017] Note 91
Beckman, H. C. Centrifugal Filters. Filtration Symposium, New York Meeting, A. C. S. 992
Bedford, C. W. and W. Scott. Reactions of Accelerators during Vulcanization. II—A Theory of Accelerators Based on the Formation of Polysulfides during Vulcanization 125
  and L. B. Sebrell. Reactions of Accelerators during Vulcanization. III—Carbo-Sulfhydryl Accelerators and the Action of Zinc Oxide 1034
Behrman, A. S. Water Softening for the Manufacture of Raw Water Ice 235
Bell, J. M. and E. B. Cordon. Studies on the Nitrotoluenes. VI—The Three-Component System: *o*-Nitrotoluene, *p*-Nitrotoluene, 1,2,4-Dinitrotoluene 307
  E. B. Cordon, F. H. Spry and W. White. Studies on the Nitrotoluenes. V—Binary Systems of *o*-Nitrotoluene and Another Nitrotoluene 59
  and F. H. Spry. Studies on the Nitrotoluenes. VII—The Three-Component System: *p*-Nitrotoluene, *o*-Nitrotoluene, 1,2,4,6-Trinitrotoluene 308
Bennett, H. C. Rapid Method for Determination of Sodium Chloride in Soap 813
Bergquist, C. and W. H. Herschel. Consistency of Starch and Dextrin Pastes 703
Berry, G. M. Chronology of Iron and Steel. *Compiled* by Goodale; *edited* by Speer. (Book Review) 745
Bingham, E. C. Adoption by the Colleges of Standard Metric Unit. New York Meeting, A. C. S. (*Addendum*, 1167) 1068
  Report of Metric System Committee. Rochester Meeting, A. C. S. 401
Binnall, F. C. The Dayton Process 242
Binns, C. F. The New Stone Age, by Howe. (Book Review) 584
Bird, E. H. and F. W. Sperr, Jr. By-Product Coking. Fuel Symposium, Chicago Meeting, A. C. S. 26
Black, R. S. and C. Pfanstiehl. Rare Sugars: Their Purity and Tests 685
Blair, A. A. Rapid Methods for the Chemical Analysis of Special Steels, Steel Making Alloys, Their Ores, and Graphites, by Johnson. (Book Review) 497
Blanco, G. W. and E. C. Sherrard. Preparation and Analysis of a Cattle Food Consisting of Hydrolyzed Sawdust 61
Bleininger, A. V. Ceramics: A Manual for Chemists, Engineers, and Manufacturers, by Malinovsky. (Book Review) 969
Blum, W. Modern Electroplater, by Coggeshall. (Book Review) 179
Bodansky, M. Determination of Small Quantities of Zinc 696
Boettner, F. and G. C. Bailey. Production of Coumarins from Maleic and Malic Acids 905
Bohn, R. T., G. L. Kelley, J. A. Wiley and W. C. Wright. Determination of Vanadium and Chromium in Ferrovanadium by Electrometric Titration 939
Bonney, R. D. and W. F. Whitescarver. Direct Identification of Soy-Bean Oil. [*See* This Journal, **12** (1920), 1174] 574
Born, S. Oil-Field Practice in Handling Crude Oil Emulsion. (Abstract) Emulsification Symposium, New York Meeting, A. C. S. 1013
Bosart, L. W. Need of a New Table for Specific Gravity and Per cent of Glycerol 944
Boyd, T. A. Motor Fuel from Vegetation 836
Bragdon, C. R. Les Vernis, by Coffignier. (Book Review) 745
Breckenridge, J. E. Boron in Relation to the Fertilizer Industry 324
Brewster, J. F. and W. G. Raines, Jr. Effect of Some Decolorizing Carbons upon Color and Colloids of Cane Juice 921
  Effect of Varying Hydrogen-Ion Concentration upon the Decolorization of Cane Juice with Carbon 1043
Briggs, T. R. Emulsions with Finely Divided Solids. Emulsification Symposium, New York Meeting, A. C. S. 1008
Brinsmaid, W. A Test for Annatto in Fats and Oils 216
Brinton, P. H. M.-P., F. M. Schertz, W. G. Crockett and P. P. Merkel. Modification of Dumas Method, and Application of Kjeldahl Method to Determination of Nitrogen in Nitronaphthalenes 636
Brown, O. W., C. R. Voris and C. O. Henke. A Dry Method of Preparing Lead Arsenate 531
Browne, C. A. Industrial and Agricultural Chemistry in the British West Indies, with Some Account of the Work of Sir Francis Watts, Imperial Commissioner of Agriculture 78
  Presentation of Priestley Portrait. New York Meeting, A. C. S. 879
  and C. A. Gamble. Revision of the Optical Method for Analyzing Mixtures of Sucrose and Raffinose 793
Brunskill, E. R. The Anilides of β-Oxynaphthoic Acid 309
Bryan, T. J. Report of the Division of Agricultural and Food Chemistry. New York Meeting, A. C. S. 958
Bryson, T. A. Discussion of Centrifugal Draining. Filtration Symposium. New York Meeting, A. C. S 993
Bullis, D. E. and J. S. Jones. Manganese in Commonly Grown Legumes 524
Burrell, G. A. Fuel Oil in Industry, by Andros. (Book Review) 101
  G. G. Oberfell and C. L. Voress. Charcoal Method of Gasoline Recovery. Fuel Symposium, Chicago Meeting, A. C. S. (Note) 58
Bushnell, L. S. A Fire Blanket Receptacle 1081
Bye, M. Benzyl Succinate: Preliminary Report on Its Composition, Manufacture, Properties, and Probable Therapeutic Uses 217
Byron, O. and A. P. Sachs. Camphor Substitutes in Manufacture of Celluloid 893

CAMPBELL, A. A. Filter Cloth and Its Relation to Filtration. Filtration Symposium, New York Meeting, A. C. S. 982
Campbell, R. C. Modern Leaf Type Filters. Filtration Symposium, New York Meeting, A. C. S. 1002
Capps, J. H. Determination of Metallic Aluminium and of Aluminium Oxide in Commercial Metal 808
Carr, R. H. Measuring Soil Toxicity, Acidity, and Basicity 931
Carpenter, C. D. Notes on Laboratory and Demonstration Apparatus 332
Carpenter, J. H. Applications of Maleic and Fumaric Acids and Their Salts in the Textile Industry 410
Carrier, W. H. and A. E. Stacey, Jr. Compartment Dryer. Drying Symposium, Rochester Meeting, A. C. S. 438
  Theory of Atmospheric Evaporation—With Special Reference to Compartment Dryers. Drying Symposium, Rochester Meeting, A. C. S. 432
Chamot, E. M. The Microbiology and Microanalysis of Foods, by Schneider. (Book Review) 100
Chandler, C. F. Chemistry in the United States. Address, Rochester Meeting, A. C. S. 391
  Presentation Address. Perkin Medal Award 160
Chapin, E. S. Natural Organic Colouring Matters, by Perkin and Everest. (Book Review) 274
Chapin, R. M. Improved Denigès Test for the Detection and Determination of Methanol in the Presence of Ethyl Alcohol 543
Clark, R. H. and H. I. Andrews. Tannin Content of Pacific Coast Conifers 1026
Clarke, H. T. Report of the Division of Organic Chemistry. New York Meeting, A. C. S. 958
Clemens, C. A. Application of Immersion Refractometer to Analysis of Aqueous Salt Solutions 813
Clifford, C. W. Calcium Chloride Method for the Determination of Water in Gasoline and in Certain Other Substances 628
  Solubility of Water in Gasoline and in Certain Other Organic Liquids, Determined by the Calcium Chloride Method 631
Clowes, G. H. A. Applied Colloid Chemistry—General Theory, by Bancroft. (Book Review) 967
Coates, C. E. Refining Raw Sugars without Bone-Black 147
Cochrane, D. C. Note on the Use of Potassium Permanganate in the Determination of Nitrogen by the Kjeldahl Method. [*See* This Journal, **12** (1920), 1195] 358
Cohen, P. W. and C. Baskerville. Solvents for Phosgene 333
Collatz, F. A. and C. H. Bailey. Activity of Phytase as Determined by the Specific Conductivity of Phytin-Phytase Solutions 317
  Studies of Wheat Flour Grades. I—Electrical Conductivity of Water Extracts 319

COLLINS, W. D. Definition of Limits for Impurities in Chemicals—Sulfate in Nitric Acid ... 948
  Laboratory Thermometers ... 240
  Reagent Chemicals. I—Proposed Specification for Sulfuric, Nitric, and Hydrochloric Acids, and for Ammonium Hydroxide ... 735
  Report of Committee on Guaranteed Reagents and Standard Apparatus. Rochester Meeting, A. C. S. ... 402
  Report on Standardization of Sizes and Shapes of Apparatus—I ... 1070
  Unit Weights for the Purchase of Reagents—II ... 473
CONGDON, L. A. AND C. R. STEWART. A New Qualitative Test for Sucrose in the Presence of Glucose ... 1143
CORDON, E. B. AND J. M. BELL. Studies on the Nitrotoluenes. VI—The Three-Component System: *o*-Nitrotoluene, *p*-Nitrotoluene, 1,2,4-Dinitrotoluene ... 307
  J. M. BELL, F. H. SPRY AND W. WHITE. Studies on the Nitrotoluenes. V—Binary Systems of *o*-Nitrotoluene and Another Nitrotoluene ... 59
COSTA, J. AND E. LITTLE. Rapid Iodometric Method for Determination of Chromium in Chromite ... 228
CROCKER, E. C. Experimental Study of the Significance of "Lignin" Color Reactions ... 625
CROCKETT, W. G., P. H. M.-P. BRINTON, F. M. SCHERTZ AND P. P. MERKEL. Modification of Dumas Method, and Application of Kjeldahl Method to Determination of Nitrogen in Nitronaphthalenes ... 636
CROSBY, P. A. AND R. R. MATTHEWS. Recovering Petroleum from Emulsions by Chemical Treatment. Emulsification Symposium, New York Meeting, A. C. S. ... 1015
CULBERTSON, J. B., W. H. ROSS AND J. P. PARSONS. Preparation of Ethylene by Hydrogenation of Acetylene ... 775
CURTIS, H. A. The Commercial Realization of the Low-Temperature Carbonization of Coal. Fuel Symposium, Chicago Meeting, A. C. S. ... 23

DAUB, G. AND J. A. WILSON. A Critical Study of Bating ... 1137
DAVIDSON, A. W. AND J. KENDALL. The Melting Point of Ammonium Sulfate ... 303
DAVIDSON, T. A. Study on Oil Bromide Test of Linseed Oil ... 801, 849
DAVIS, C. E. Shortening: Its Definition and Measurement ... 797
DAVIS, L. Cocoa and Chocolate—Their Chemistry and Manufacture, by Whymper. (Book Review) ... 1093
DAVIS, R. O. E. Soil Alkali, by Harris. (Book Review) ... 179
DAVIS, W. Washington Letter. 364, 486, 575, 656, 739, 850, 961, 1082, 1171
DEAN, E. W. Gasoline and Other Motor Fuels, by Ellis and Meigs. (Book Review) ... 665
  AND F. W. LANE. Viscosity-Temperature Curves of Fractions of Typical American Crude Oils ... 779
DEDLOW, C. Spare Time—A Defense. (*See* Jordan, 253, Sprague, 474) 1067
DE FAZI, R. The Action of Ultraviolet Rays on the Saccharomycetes. [*See* THIS JOURNAL, **12** (1920), 740] ... 265
DELBRIDGE, T. G. Report of Delegate to Conference Called by American Petroleum Institute, N. Y., April 11, 1921. Rochester Meeting, A. C. S. ... 403
DELONG, C. R. Chemical Industry from a Tariff Viewpoint ... 470
DENNIS, L. M. Liability for Laboratory Explosions ... 1079
DERICK, C. G. Unification des Noms des Colorants les Plus Usuels, by Sisley. (Book Review) ... 497
DERLETH, C. P. Filter Aids. Filtration Symposium, New York Meeting, A. C. S. ... 989
DEVRIES, O. Relation between Coefficient of Vulcanization and Mechanical Properties of Vulcanized Rubber ... 1133
DICKEY, G. D. Leaf and Rotary Suction Filters. Filtration Symposium, New York Meeting, A. C. S. ... 997
DONALDSON, W. Detection of Phenols in Water. (*See* Scott, 422, 574) 848
DONLEAVY, J. J. AND A. J. HILL. Alkylation of Aromatic Amines by Heating with Aliphatic Alcohols ... 504
DORAN, J. M. Alcohol and the Chemical Industries ... 564
DORE, W. H. The Estimation of Cellulose in Wood. [*See* THIS JOURNAL, **12** (1920), 264, 873] ... 358
DOREMUS, C. A. Centenary of the Founding of the Sciences of Electromagnetism and Electrodynamics ... 166
DORR, J. V. N. Plant Excursions, New York Meeting, A. C. S. ... 1170
DOWELL, C. T. AND W. G. FRIEDMANN. Note on the Use of Potassium Permanganate in the Determination of Nitrogen by the Kjeldahl Method. [*See* THIS JOURNAL, **12** (1920), 1195] ... 358
DRINKER, P. European Practice in Cellulose Acetate and Dopes during the War ... 831
DUBOIS, G. Special Cost Factors and Their Relation to the Development of Our Organic Chemical Industry ... 1159
DUTCHER, R. A. Factors Influencing the Vitamine Content of Foods. Vitamine Symposium, New York Meeting, A. C. S. ... 1102

EDDY, W. G. AND H. C. Discussion on Electrical Dehydration of Crude Oil. Emulsification Symposium, New York Meeting, A. C. S. ... 1016
ELLIOTT, F. A. AND S. E. SHEPPARD. Gold Number of Commercial Gelatins ... 699
EMERY, W. O. Studies in Synthetic Drug Analysis. VIII—Estimation of Salicylates and Phenol ... 538
EMMETT, A. D. Standardized Feeding Methods for the Study of Vitamines. Vitamine Symposium, New York Meeting, A. C. S. ... 1104
ESSELEN, G. J., JR. Les Éthers Cellulosiques; Première Partie, Les Éthers Minéraux de la Cellulose, by Dubosc. (Book Review) ... 584
  Report of the Section of Cellulose Chemistry. New York Meeting, A. C. S. ... 959
EVANS, P. N. Vapor Composition of Alcohol-Water Mixtures. [*See* THIS JOURNAL, **12** (1920), 496] ... 168
EVERS, E. W. AND G. L. KELLEY. Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis ... 1052

FARAGHER, W. F., W. A. GRUSE AND F. H. GARNER. The Iodine Number of Unsaturated Hydrocarbons and Cracked Gasolines ... 1044
FARNAU, E. F. AND H. J. WITTEVEEN. Colors Developed by Cobalt Oxides ... 1061
FARR, H. V., A. E. STEARN AND N. P. KNOWLTON. An Investigation of the U. S. P. Assay for Phosphoric Acid and Soluble Phosphates ... 220
FAY, H. Metallography, Part II. The Metals and Common Alloys, by Hoyt. (Book Review) ... 856
FELDSTEIN, L. AND R. S. HILTNER. Composition of Hollyhock Seed and Oil ... 635
FELLERS, C. R. Soy-Bean Oil: Factors Which Influence Its Production and Composition ... 689
FEUER, B. AND F. W. TANNER. The Action of Ultraviolet Rays on the Saccharomycetes. [*See* THIS JOURNAL, **12** (1920), 740] ... 265
FIELD, E. AND L. H. ALMY. Preservation of Fish Frozen in Chilled Brine. I—Penetration of Salt ... 927
FIELDNER, A. C. Fuel Production and Utilization, by Taylor. (Book Review) ... 494
  Technical Gas and Fuel Analysis, by White. (Book Review) ... 180
  A. A. STRAUB AND G. W. JONES. Gasoline Losses Due to Incomplete Combustion in Motor Vehicles. Fuel Symposium, Chicago Meeting, A. C. S. ... 51
FINCH, E. E. Pulp or Filter Mass Filters. Filtration Symposium, New York Meeting, A. C. S. ... 996
FINK, C. G. The Manufacture of Chemicals by Electrolysis, by Hale. (Book Review) ... 274
FISHER, H. L., H. GRAY AND R. MERLING. Discussion of the Tetrabromide Method for Estimating Rubber Hydrocarbon ... 1031
FLEMING, R. M., C. J. HUMPHREY AND E. BATEMAN. Studies on the Toxicity of Wood Preservatives—III ... 618
FLEMING, R. S. Spray Process of Drying. Drying Symposium, Rochester Meeting, A. C. S. ... 447
FLOWER, A. H., G. D. KRATZ AND B. J. SHAPIRO. Action of Certain Organic Accelerators in Vulcanization of Rubber—II, 67; III ... 128
FLURY, C. Repairing Iron Leaching Vats ... 168
FRANCIS, C. K. American Lubricants, by Lockhart. (Book Review) ... 496
FRASER, T. AND H. F. YANCEY. The Distribution of the Forms of Sulfur in the Coal Bed. Fuel Symposium, Chicago Meeting, A. C. S. ... 35
FRED, E. B. AND W. H. PETERSON. Fermentation Process for the Production of Acetic and Lactic Acids from Corncobs ... 211
  W. H. PETERSON AND J. H. VERHULST. Fermentation Process for Production of Acetone, Alcohol, and Volatile Acids from Corncobs ... 757
FRIEDMANN, W. G. AND C. T. DOWELL. Note on the Use of Potassium Permanganate in the Determination of Nitrogen by the Kjeldahl Method. [*See* THIS JOURNAL, **12** (1920), 1195] ... 358
FRIES, A. A. La Chimie et La Guerre, by Moureu. (Book Review) ... 1092
FRY, W. H., C. J. MOORE AND H. E. MIDDLETON. Methods for Determining the Amount of Colloidal Material in Soils ... 527
FUNK, C. The Antiberiberi Vitamine. Vitamine Symposium, New York Meeting, A. C. S. ... 1110

GAMBLE, C. A. AND C. A. BROWNE. Revision of the Optical Method for Analyzing Mixtures of Sucrose and Raffinose ... 793
GARNER, F. H., W. F. FARAGHER AND W. A. GRUSE. The Iodine Numbers of Unsaturated Hydrocarbons and Cracked Gasolines ... 1044
GARNER, J. B. Enrichment of Artificial Gas with Natural Gas. Fuel Symposium, Chicago Meeting, A. C. S. ... 58
GARVAN, F. P. Chemistry and the State. Address, New York Meeting, A. C. S. ... 866
GILL, A. H. Ignition of Fire Engine Hose When in Use ... 168
  Rubber, Resins, Paints and Varnishes, by Morrell. (Book Review) ... 856
  AND H. S. SIMMS. Microanalytical Methods in Oil Analysis ... 547
GILLETTE, H. C. Industrial Gases, by Greenwood. (Book Review) ... 181
GLAZE, F. W. Determination of Small Amounts of Lead in Brass ... 553
GORDON, N. E. Report, Section of Chemical Education. New York Meeting, A. C. S. ... 959
GORE, H. C. AND C. E. MANGELS. Effect of Heat on Different Dehydrated Vegetables ... 525
  Relation of Moisture Content to the Deterioration of Raw-Dried Vegetables upon Common Storage ... 523
GORTNER, R. A. The Determination of Hydrogen Ions, by Clark. (Book Review) ... 373
GOSS, B. C. Gas Warfare, by Farrow. (Book Review) ... 495
GRABER, H. T. Chemistry of Enzyme Actions, by Falk. (Book Review) ... 372
  Standardization of Rare Sugars ... 687
GRAY, F. J., W. H. MACINTIRE AND W. M. SHAW. The Non-Biological Oxidation of Elementary Sulfur in Quartz Media ... 310
GRAY, G. W. Technical Examination of Crude Petroleum, Petroleum Products and Natural Gas, by Hamor and Padgett. (Book Review) ... 662
GRAY, H., H. L. FISHER AND R. MERLING. Discussion of the Tetrabromide Method for Estimating Rubber Hydrocarbon ... 1031
GREEN, H. Recent Development in Art of Rubber Microsectioning ... 1130
  Volume Increase of Compounded Rubber under Strain. [*See* Schippel, THIS JOURNAL, **12** (1920), 33] ... 1029
GRIGGS, M. A. The Alkaline Hydrolysis of Casein ... 1027
GROSS, P. AND A. H. WRIGHT. Distillation Apparatus ... 701
GROTLISCH, V. E. AND W. C. SMITH. Detection and Estimation of Coal-Tar Oils in Turpentine ... 791
GRUSE, W. A. Report, Section of Petroleum Chemistry. New York Meeting, A. C. S. ... 959
  W. F. FARAGHER AND F. H. GARNER. The Iodine Numbers of Unsaturated Hydrocarbons and Cracked Gasolines ... 1044
GURNEY, H. P. Modulus of Hardness of Vulcanized Rubber ... 707

HAAG, I. L. AND J. H. REEDY. The Preparation and Instability of Tricalcium Arsenate ... 1038
HAHN, D. A. AND H. E. HOLMES. Chemistry of Acenaphthene and Its Derivatives ... 822
HALE, W. J. Immediate Needs of Chemistry in America. Address, Rochester Meeting, A. C. S. ... 460
HANSON, H. H. Chemistry of Pulp and Paper Making, by Sutermeister. (Book Review) ... 583
HARRINGTON, J. W. Chemistry's Greatest Rally ... 733
  Rochester Ready for Chemical Cohorts ... 352
HARRIS, J. B. Determination of Reducing Sugars in Lead-Preserved Cane Juices ... 925
HARVEY, M. AND L. H. BAEKELAND. Further Studies on Phenolic Hexamethylenetetramine Compounds ... 135
HASLAM, R. T. A Text Book of Chemical Engineering, by Hart. (Book Review) ... 495
  School of Chemical Engineering Practice of Massachusetts Institute of Technology ... 465
HASTINGS, E. G. Constant Temperature Rooms ... 1056
HAWLEY, L. F. Production of Artificially Dense Charcoal ... 301
HAWLEY, R. C. Forests of the United States as a Source of Liquid Fuel Supply ... 1059
HEISIG, H. M. AND J. A. WILSON. Role of Acidity in Dehydration of Sewage Sludge ... 406
HENKE, C. O., O. W. BROWN AND C. R. VORIS. Dry Method of Preparing Lead Arsenate ... 531
HERSCHEL, W. H. AND C. BERGQUIST. Consistency of Starch and Dextrin Pastes ... 703

Herty, C. H. Report, Committee on an Institute for Chemo-Medical Research. Rochester Meeting, A. C. S. 403
Report, Committee to Coöperate with Chemical Warfare Service. Rochester Meeting, A. C. S. 403
Editorials:
A Call to Service 503
A Fireside Chat 1198
Aftermath 187
Alcoholic Tribulations 591
Amenities de Luxe 3
An Acknowledgment 750
An Anomaly 378
A Nation's Loss 974
Appreciations 188
Are Your Folks on the List? 3
A Special Problem 188
A Time for Gathering 670
A Tragedy Averted 502
Congressional Recognition of Chemistry 592
Danger Ahead 974
Death of Lord Moulton 284
Echoes from the 66th Congress 282
Effective Help 751
Elementary Economics 107
Equitable Distribution 5
Every Man's Job 975
Expansion for the News Service 4
Experimental Evidence 752
Facts Supplant General Statements. (*See* "Thinking It Through," 186) 590
Fair Weather Predictions 590
From the Tower 865
Have You Done Your Share? 670
Less Legislation—More Coöperation 503
Notes 5, 405, 975
No Time for Dullness 4
Officers for 1921 2
On to Rochester 282
Restoration in Poland 671
Sowing Good Seed 109
Specific Facts 283
Square Dealing 974
The Chemist and the Railways 591
The Fight in the Senate 750
The Meeting and the Exposition 752
The Passing of Secrecy 751
The President Takes a Hand 752
The Race Is Not Always to the Swift 109
The Road to Demoralization 108
Thinking It Through. (*See* "Facts Supplant General Statements," 590) 186
Thoughts Translated into Deeds 108
Vicarious Punishment 187
Welcome to Madame Curie 502
Welcome to Our Visitors 750
When a Law Defeats Itself—Repeal It 3
Will the Senate Act? 2
Your Brother's Keeper 187
Hess, A. F. The Antiscorbutic Vitamine. Vitamine Symposium, New York Meeting, A. C. S. 1115
Hibbert, H. Role of the Chemist in Relation to Future Supply of Liquid Fuel 841
Studies on the Chemistry of Cellulose. I—The Constitution of Cellulose 256, 334
Hickey, G. M. The Use of Filter-Cel for Industrial Filtration Processes. Filtration Symposium, New York Meeting, A. C. S. 990
Hill, A. J. and J. J. Donleavy. Alkylation of Aromatic Amines by Heating with Aliphatic Alcohols. 504
Hillebrand, W. F. Samuel Stockton Voorhees. Obituary 1085
Hiltner, R. S. and L. Feldstein. Composition of Hollyhock Seed and Oil 635
Hinckley, C. E. and R. P. Anderson. Gasoline from Natural Gas. V—Hydrometer for Small Amounts of Gasoline 144
Hirsh, M. and C. Baskerville. Rate of Evaporation of Ethyl Chloride from Oils 322
Hoffman, J. I. and G. E. F. Lundell. Determination of Cobalt and Nickel in Cobalt Steels 540
Holmes, H. E. and D. A. Hahn. Chemistry of Acenaphthene and Its Derivatives 822
Holmes, H. N. Colloid Development 357
Holmes, W. C., H. Rogers and W. L. Lindsay. Melting Point of Diphenylamine 314
Hoover, C. R. Detection of Carbon Monoxide 770
Hopkins, O. P.:
Chemical Industry and Trade of France 6
Chemical Industry and Trade of England 189
Chemical Industry and Trade of Switzerland 285
Chemical Industry and Trade of Holland 593
Our Foreign Trade in Chemicals 753
Horne, W. D. Manufacture of Sugar from the Cane and the Beet, by Heriot. (Book Review) 277
Horsch, W. G., R. E. Wilson and M. A. Youtz. Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese. (*Correction*, 960) 763
Horton, P. M. Preparation of Mannose from Ivory-Nut Shavings 1040
Hortvet, J. Cryoscopy of Milk 198
Howard, H. C. Comparative Study of Vibration Absorbers 231
Howe, H. E. Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. (Book Review) 1091
Division of Industrial and Engineering Chemistry—Submittal of Papers 570
Report, Division of Industrial and Engineering Chemistry. New York Meeting, A. C. S. 956
Hudson, C. S. Simple Carbohydrates and the Glucosides, by Armstrong. (Book Review) 276
Huff, W J. Dehydration of Tar in the Laboratory 1123
Humphrey, C. J. Traité de la Conservation et de l'Amelioration des Bois (Treatise on the Preservation and Improvement of Wood), by Keghel. (Book Review) 969
R. M. Fleming and E. Bateman. Studies on the Toxicity of Wood Preservatives—III 618
Hursh, R. K., C. W. Parmelee and E W. Washburn. A Selected Bibliography of Books, in the English Language, Dealing with Ceramic Chemistry and the Ceramic Industries 476
Hussey, R. E. and B. Mears. The Use of Perchloric Acid as an Aid to Digestion in the Kjeldahl Nitrogen Determination 1054

Jackson, D. D. and J. J. Morgan. Application of the Vapor Pressures of Potassium Compounds to the Study of the Recovery of Potash by Volatilization 292
Measurement of Vapor Pressures of Certain Potassium Compounds 110
Jarrell, T. D. and F. P. Veitch. Water Resistance of Treated Canvas during Continuous Exposure to Weather 672
Johnsen, B. Estimation of Cellulose in Wood. [*See* This Journal, **12** (1920), 264, 873] 358
Johnson, E. Determination of Dicyanodiamide and of Urea in Fertilizers 533
Jones, G. W., A. C. Fieldner and A. A. Straub. Gasoline Losses Due to Incomplete Combustion in Motor Vehicles. Fuel Symposium, Chicago Meeting, A. C. S. 51
and W. L. Parker. The Formation of Oxides of Nitrogen in the Slow Combustion and Explosion Methods in Gas Analysis 1154
Jones, J. S. and D. E. Bullis. Manganese in Commonly Grown Legumes 524
Jordan, H. W. Biological Trend of Industry 650
Crowds and Their Manners 566
Food and Shelter 1161
Labor's Crisis, by Mendelsohn. (Book Review) 665
Method for Social Research 1066
Out-of-Door Education for the Chemist 731
Science of Human Engineering 844
Social Industrial Relations 473
Social Research 949
Spare Time. (*See* Sprague, 474; Joyce, 651; Dedlow, 1067) 253
Jordan, W. L. Continuous Sampling of Sugar Liquors 640
Joyce, A. W. Dyes Derived from Beta-Oxynaphthoic Acid and from J-Acid, with Reference to Chemical Foundation Patents 946
Joyce, C. M. Spare Time. (*See* Jordan, 253; Sprague, 474; Dedlow, 1067) 651
Joyce, C. M. and C. Baskerville. Regenerating Bookstock 214

Kandell, M. and J. E. Zanetti. Formation of Anthracene from Benzene and Ethylene. (*Correction*, 358) 208
Kendall, J. and A. W. Davidson. Melting Point of Ammonium Sulfate 303
Kelley, G. L. and E. W. Evers. Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis 1052
and J. A. Wiley. Determination of Chromium in Ferrochromium by Electrometric Titration 1053
J. A. Wiley, R. T. Bohn and W. C. Wright. Determination of Vanadium and Chromium in Ferrovanadium by Electrometric Titration 939
Kelly, M. W. and A. W. Thomas. The Effect of Concentration of Chrome Liquor upon the Adsorption of Its Constituents by Hide Substance 65
Kern, E. J. and J. A. Wilson. Color Value of a Tan Liquor as a Function of the Hydrogen-Ion Concentration 1025
Determination of Tannin 772
Keyes, H. E. and H. V. Tartar. The Electrical Conductivity of Solutions of Zinc Sulfate in the Presence of Sulfuric Acid 1127
Kiplinger, C. C. Modified Laboratory Apparatus 713
Knowlton, N. P., H. V. Farr and A. E. Stearn. Investigation of the U. S. P. Assay for Phosphoric Acid and Soluble Phosphates 220
and H. C. Mounce. Revised Specific Gravity Table for Orthophosphoric Acid at 25°/25° C. 1157
Koch, M. L. and A. T. Shohl. Combined Extractor, Reflux Condenser, Still and Autoclave 819
Kohman, E. F. Discoloration in Canned Sweet Potatoes 634
Kratz, G. D., A. H. Flower and B. J. Shapiro. Action of Certain Organic Accelerators in the Vulcanization of Rubber—II, 67; III, 128
Kreisinger, H. By-Product Coke, Anthracite, and Pittsburgh Coal as Fuel for Heating Houses. Fuel Symposium, Chicago Meeting, A. C. S. 31
Kremers, H. C. Electric Muffle Furnaces for Laboratory Use 561

Lachman, A. Rapid Volumetric Method for Determining Alcohol 230
Ladd, E. F. Papers on Paint and Varnish, by Gardner. (Book Review) 497
LaForge, F. B. Production of Furfural by the Action of Superheated Water on Aqueous Corncob Extract 1024
Lamb, A. B. Nitrogen Supply of the World 1166
LaMer, V. K. Vitamines from the Standpoint of Physical Chemistry. Vitamine Symposium, New York Meeting, A. C. S. 1108
Lane, F. W. and E. W. Dean. Viscosity-Temperature Curves of Fractions of Typical American Crude Oils 779
Lavett, C. O. and D. J. VanMarle. Vacuum Drying. Drying Symposium, Rochester Meeting, A. C. S. 600
Layng, T. E. and S. W. Parr. Low-Temperature Carbonization and Its Application to High Oxygen Coals. Fuel Symposium, Chicago Meeting, A. C. S. (*Correction*, 266) 14
Lee, H. R. Contribution to the Estimation of H-Acid 1049
Lenher, V. Dictionary of Chemical Solubilities—Inorganic, by Comey and Hahn. (Book Review) 662
Lenroot, I. L. Relation of Our Chemical Industry to Our National Defense. Address, Chemical Exposition 888
Lewis, H. B. Report of the Division of Biological Chemistry. New York Meeting, A. C. S. 958
Lewis, W. K. Rate of Drying of Solid Materials. Drying Symposium, Rochester Meeting, A. C. S. 427
Vapor Composition of Alcohol-Water Mixtures. [*See* This Journal, **12** (1920), 496] 168
Lichthardt, G. H. P. Cold Test Apparatus for Oils 145
Lindsay, C. F. Hotel Accommodations, A. C. S. Meeting, New York City, September 6 to 10, 1921 571
Lindsay, W. L., H. Rogers and W. C. Holmes. Melting Point of Diphenylamine 314
Linz, A. Phthalic Anhydride Derivatives. (*See* Phillips, 247) 363
Little, A. D. Place of Chemistry in Business. Address, Rochester Meeting, A. C. S. 386
Willis R. Whitney. Perkin Medal Award 158
Little, E. and J. Costa. Rapid Iodometric Method for Determination of Chromium in Chromite 228
Livermore, W. D. Application of Dyestuffs, by Matthews. (Book Review) 99
Loevenhart, A. S. Introduction to Chemical Pharmacology, by McGuigan. (Book Review) 585

Longworth, N. American Chemical Industry and Its Need for Encouragement and Protection. Address, Rochester Meeting, A. C. S. 384
Lormand, C. Paris Letter. 94, 171, 269, 366, 576, 657, 852, 962, 1083, 1172
  Second International Chemical Conference 737
Lukens, H. S. New Type of Electrolytic Cell 562
Lundell, G. E. F. and J. I. Hoffman. Determination of Cobalt and Nickel in Cobalt Steels 540
Lyder, E. E. and R. H. McKee. Thermal Decomposition of Shales. I—Heat Effects 613
  Thermal Decomposition of Oil Shales. II—Determination of Heat of Reaction Involved in Their Thermal Decomposition 678

MACINTIRE, W. H., F. J. Gray and W. M. Shaw. Non-Biological Oxidation of Elementary Sulfur in Quartz Media 310
MacKay, G. M. J. Nature of Animal Light, by Harvey. (Book Review) 180
Mahood, S. A. Estimation of Cellulose in Wood. [*See* This Journal, **12** (1920), 264, 873] 358
Mangels, C. E. Mineral Constituents of Potatoes and Potato Flour: Effect of Process of Manufacture on Composition of Ash of Potato Flour 418
  and H. C. Gore. Effect of Heat on Different Dehydrated Vegetables 525
    Relation of Moisture Content to the Deterioration of Raw-Dried Vegetables upon Common Storage 523
Marsh, L. G. Possible Uses of Corncob Cellulose in the Explosives Industry 296
Matthews, R. R. Determination of Chlorides in Petroleum 325
  and P. A. Crosby. Recovering Petroleum from Emulsions by Chemical Treatment. Emulsification Symposium, New York Meeting, A. C. S. 1015
McBride, R. S. Report, Symposium on Chemistry of Gases and Fuel. New York Meeting, A. C. S. 956
McCallum, S. T. Preparation of Alcoholic Potassium Hydroxide Volumetric Solution 943
McElroy, K. P. Our Anomalous Patent Office 469
McIlhiney, P. C. Technical Methods of Analysis. *Edited* by Griffin. (Book Review) 745
McKee, R. H. and E. E. Lyder. Thermal Decomposition of Shales. I—Heat Effects 613
  Thermal Decomposition of Oil Shales. II—Determination of Heat of Reaction Involved in Their Thermal Decomposition 678
Meade, G. P. Dry Substance in Molasses, Sirups and Juices by Spencer Electric Oven 924
  Examination of Sugar Crystals by Projection 712
Meade, R. K. Some New Features in Limekiln Construction 722
Mears, B. and R. E. Hussey. Use of Perchloric Acid as an Aid to Digestion in the Kjeldahl Nitrogen Determination 1054
Meeker, G. H. Laboratory Manual for the Detection of Poisons and Powerful Drugs, by Autenrieth. (Book Review) 663
Mees, C. E. K. Measurement of Color 729
Merchant, E. H. Assignment of Patents. (*See* Note, 646) 849
Merkel, P. P., P. H. M.-P. Brinton, F. M. Schertz and W. G. Crockett. Modification of Dumas Method, and Application of Kjeldahl Method to Determination of Nitrogen in Nitronaphthalenes 636
Merling, R., H. L. Fisher and H. Gray. Discussion of the Tetrabromide Method for Estimating Rubber Hydrocarbon 1031
Merz, R. G. Direct Heat Rotary Drying Apparatus. Drying Symposium, Rochester Meeting, A. C. S. 449
Meyers, S. L. Water Heater for Analytical Work 563
Miall, S. London Letter 94, 365, 576, 740, 851, 1084
Middleton, H. E., C. J. Moore and W. H. Fry. Methods for Determining the Amount of Colloidal Material in Soils 527
Miller, E. J., C. S. Robinson and O. B. Winter. Studies of Availability of Organic Nitrogenous Compounds—I 933
Miner, E. G. Address of Welcome. Rochester Meeting, A. C. S. 380
Minor, J. E. Cellulose Mucilage 131
Monroe, K. P. Preparation and Technical Uses of Furfural 133
Moore, C. J., W. H. Fry and H. E. Middleton. Methods for Determining the Amount of Colloidal Material in Soils 527
Moore, H. C. Report of the Division of Fertilizer Chemistry. New York Meeting, A. C. S. 957
Morgan, J. J. New Method for the Determination of Potassium in Silicates 225
  and D. D. Jackson. Application of the Vapor Pressures of Potassium Compounds to the Study of the Recovery of Potash by Volatilization 292
    Measurement of Vapor Pressures of Certain Potassium Compounds 110
Morrison, H. A. Oliver Continuous Filters. Filtration Symposium, New York Meeting, A. C. S. 1005
Mounce, H. C. and N. P. Knowlton. Revised Specific Gravity Table for Orthophosphoric Acid at 25°/25° C. 1157
Mueller, E. F. and C. W. Waidner. Note on Partial and Total Immersion Thermometers 237
Munroe, C. E. Technical Records of Explosives Supply, 1915–1918. I—Denitration of Spent Acids. II—Manufacture of Trinitrotoluene (TNT). (Book Review) 1176

NEWHALL, C. A. The Direct Identification of Soy-Bean Oil. [*See* This Journal, **12** (1920), 1174] 574
Nichols, W. H. European Relief Council. (Note) 169
Northrup, E. F. Uniform High Temperature throughout a Large Volume 639
Norton, S. G. Use of Nitroglycerin Spent Acid as Charging Acid for Nitric Acid Stills 677

OBERFELL, G. G., G. A. Burrell and C. L. Voress. Charcoal Method of Gasoline Recovery. Fuel Symposium, Chicago Meeting, A. C. S. (Note) 58
Okuda, Y. and H. F. Zoller. Relations of Hydrogen-Ion Concentration to the Heat Coagulation of Proteins in Swiss Cheese Whey 515
Olsen, J. C. Meeting of the Section of Chemical Education 1074
  Reports of American Institute of Chemical Engineers:
    13th Annual Meeting, New Orleans, December 6 to 9, 1920 89
    13th Semiannual Meeting, Detroit, June 20 to 25, 1921 652

PARKER, W. L. and G. W. Jones. The Formation of Oxides of Nitrogen in the Slow Combustion and Explosion Methods in Gas Analysis 1154
Parkinson, N. A. Government Publications 97, 175, 271, 369, 490, 580, 659, 742, 854, 964, 1087, 1174
  1921 Meeting of the Association of Official Agricultural Chemists .. 1168
Parmelee, C. W., E. W. Washburn and R. K. Hursh. Selected Bibliography of Books, in the English Language, Dealing with Ceramic Chemistry and the Ceramic Industries 476
Parr, S. W. with M. M. Austin. Potash Shales of Illinois 1144
  and T. E. Layng. Low-Temperature Carbonization and Its Application to High Oxygen Coals. Fuel Symposium, Chicago Meeting, A. C. S. (*Correction*, 266) 14
Parsons, C. L. Membership Directory of the Society 737
Parsons, J. P., W. H. Ross and J. B. Culbertson. Preparation of Ethylene by Hydrogenation of Acetylene 775
Parsons, L. W. and O. G. Wilson, Jr. Some Factors Affecting the Stability and Inversion of Oil-Water Emulsions. Emulsification Symposium, New York Meeting, A. C. S. 1116
Patterson, A. M. Dictionary of Chemical Terms, by Couch. (Book Review) 583
Peterson, A. C. and C. H. Bailey. Studies of Wheat Flour Grades. II—Buffer Action of Water Extracts. (*See* Bailey and Collatz, 319) 916
Peterson, W. H. and E. B. Fred. Fermentation Process for the Production of Acetic and Lactic Acids from Corncobs 211
  E. B. Fred and J. H. Verhulst. Fermentation Process for Production of Acetone, Alcohol, and Volatile Acids from Corncobs 757
Pfanstiehl, C. and R. S. Black. Rare Sugars: Their Purity and Tests 685
Phillips, M. Alkali Fusions. III—Fusion of Phenylglycine-*o*-Carboxylic Acid for Production of Indigo 759
  Phthalic Anhydride Derivatives. (*See* Linz, 363) 247
Pickard, G. H. Tables of Refractive Indices. II—Oils, Fats and Waxes. *Compiled* by Kanthack; *edited* by Goldsmith. (Book Review) 1092
Pierce, E. L. John Downer Pennock. Obituary 489
Pope, W. J. Modern Developments in War Making. Address, New York Meeting, A. C. S. 874
Porter, H. C. Fuel Conservation, Present and Future. Fuel Symposium, Chicago Meeting, A. C. S. 47
Potvliet, M. Comparison of Results in Desugarization with the Steffen Lime, Barium, and Strontium Processes 1041
Powell, A. R. Low-Temperature Carbonization and Its Application to High Oxygen Coals. (*See* Parr and Layng, 14) *Correction* 266
  Some Factors Affecting the Sulfur Content of Coke and Gas in the Carbonization of Coal. Fuel Symposium, Chicago Meeting, A. C. S. 33

RABAK, F. Grape-Seed Oil 919
  Yield and Composition of Wormwood Oil from Plants at Various Stages of Growth during Successive Seasons 536
Raines, W. G., Jr. and J. F. Brewster. Effect of Some Decolorizing Carbons upon Color and Colloids of Cane Juice 921
  Effect of Varying Hydrogen-Ion Concentration upon the Decolorization of Cane Juice with Carbon 1043
Ransom, J. H. Copper Refining, by Addicks. (Book Review) 857
Ray, A. B. Incendiaries in Modern Warfare 641, 714
Read, J. W. Rapid Dry Combustion Method for the Simultaneous Determination of Soil Organic Matter and Organic Carbon 305
Reedy, J. H. and I. L. Haag. The Preparation and Instability of Tricalcium Arsenate 1038
Rhodehamel, H. W. and E. H. Stuart. Atropine Sulfate from *Datura stramonium* 218
Richards, J. W. Reports of American Electrochemical Society:
  39th Meeting, Atlantic City, N. J., April 21 to 23, 1921 483
  40th Meeting, Lake Placid, N. Y., September 29 to October 1, 1921 ... 1076
Richardson, W. D. Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, by Doolittle, *et al.* (Book Review) 496
Richter, G. A. Combustion Smokes 343
Ridley, G. B. Tunnel Dryers. Drying Symposium, Rochester Meeting, A. C. S. 453
Robinson, Charles S., O. B. Winter and E. J. Miller. Studies of Availability of Organic Nitrogenous Compounds—I 933
Robinson, Clark S. Radiation Effects in Thermometry 820
Rodman, C. J. Determination of Moisture in Insulating Oils 1149
Rogers, A. Dictionary of Applied Chemistry, Vol. I, by Thorpe. (Book Review) 664
Rogers, H., W. C. Holmes and W. L. Lindsay. Melting Point of Diphenylamine 314
Rose, R. E. American Chemistry, by Hale. (Book Review) 857
  Chemistry and Technology of the Diazo-Compounds, by Cain. (Book Review) 583
Ross, W. H., J. B. Culbertson and J. P. Parsons. Preparation of Ethylene by Hydrogenation of Acetylene 775
Ruttan, R. F. Plan for the Development of Industrial Research in Canada. Address, New York Meeting, A. C. S. 876

SABIN, A. H. Analysis of Paint Vehicles, Japans, and Varnishes, by Holley. (Book Review) 101
  Thomas Lynton Briggs. Obituary 489
Sachs, A. P. and O. Byron. Camphor Substitutes in Manufacture of Celluloid 893
Sadtler, S. P. Industrial Organic Analysis, by Arup. (Book Review) 276
Schaal, R. B. Simple Method for Determination of Vanadium in Ores and Metallurgical Products 698
Schertz, F. M., P. H. M.-P. Brinton, W. G. Crockett and P. P. Merkel. Modification of Dumas Method, and Application of Kjeldahl Method to Determination of Nitrogen in Nitronaphthalenes 636
Schmitz, H. and S. M. Zeller. Toxicity of Various Fractions and Combinations of Fractionsof Coal-Tar Creosote to Wood-Destroying Fungi 621
Schrero, M. Apparatus for Rapid Determination of Available Chlorine in Bleach Liquor 559
Scott, R. D. Detection of Phenols in Water. (*See* Donaldson and Trowbridge, 848) (*Correction*, 574) 422
  and E. G. Will. Cider Preservatives 1141
Scott, W. and C. W. Bedford. Reactions of Accelerators during Vulcanization. II—A Theory of Accelerators Based on the Formation of Polysulfides during Vulcanization 125
Sebrell, L. B. and C. W. Bedford. Reactions of Accelerators during Vulcanization. III—Carbo-Sulfhydryl Accelerators and the Action of Zinc Oxide 1034

Seidell, A. Chemistry of Vitamines........ 72
Experiments on the Isolation of the Antineuritic Vitamine. Vitamine Symposium, New York Meeting, A. C. S........ 1111
Vitamines—Essential Food Factors, by Harrow. (Book Review)........ 584
Senseman, C. E. Benzenedisulfonic Acid from Benzene Monosulfonic Acid........ 1124
Shapiro, B. J., A. H. Flower and G. D. Kratz. Action of Certain Organic Accelerators in the Vulcanization of Rubber—II, 67; III........ 128
Shaw, J. A. Method for the Determination of Free and Combined Carbon Dioxide........ 1151
Shaw, W. M., W. H. MacIntire and F. J. Gray. Non-Biological Oxidation of Elementary Sulfur in Quartz Media........ 310
Sheppard, S. E. Colloidal Fuels, Their Preparation and Properties. Fuel Symposium, Chicago Meeting, A. C. S........ 37
Removal of Free Acid from Nitrocellulose with Special Reference to the Use of Saline Leaches........ 1017
Report of the Division of Physical and Inorganic Chemistry. New York Meeting, A. C. S........ 956
and F. A. Elliott. Gold Number of Commercial Gelatins........ 699
and S. Sweet. Setting and Melting Points of Gelatins........ 423
Sherrard, E. C. and G. W. Blanco. Preparation and Analysis of a Cattle Food Consisting of Hydrolyzed Sawdust........ 61
Sherrick, J. L. Emulsifying Agents in Oil-Field Emulsions. Emulsification Symposium, New York Meeting, A. C. S........ 1010
Sherrill, E. Centrifugal Method for Determining Potash. (*Correction*, 480)........ 227
Sherwood, S. F. Process for Producing Palatable Sirup from Sugar Beets........ 799
Shinn, O. L. Determination of Volatile Matter in Graphite........ 633
Shoaff, P. S. and J. W. Turrentine. Potash from Kelp. IV—Continuous Countercurrent Lixiviation of Charred Kelp........ 605
Shohl, A. T. and M. L. Koch. Combined Extractor, Reflux Condenser, Still and Autoclave........ 819
Shreve, R. N. Action of Lime on Greensand........ 693
Report, Division of Dye Chemistry. New York Meeting, A. C. S. 958
Sibley, R. L. Effect of Certain Fire-Proofing Solutions on Cotton Fabric........ 676
Simms, H. S. Determination of Refractive Indices of Oils........ 546
and A. H. Gill. Microanalytical Methods in Oil Analysis........ 547
Simpson, S. G. The Effect of the Presence of Filter Paper on Permanganate-Oxalate Titrations........ 1152
Skinner, W. W. Report of the Division of Water, Sewage and Sanitation. New York Meeting, A. C. S........ 959
Smalley, F. N. Coöperative Analytical Work of the American Oil Chemists' Society........ 655
Smith, A. H. Report of the Division of Rubber Chemistry. New York Meeting, A. C. S........ 957
Smith, E. F. Message of Welcome and Call to Duty. New York Meeting, A. C. S........ 844
Research. Address........ 254
Smith, W. C. and V. E. Grotlisch. Detection and Estimation of Coal-Tar Oils in Turpentine........ 791
Spence, D. Estate Rubber: Its Preparation, Properties and Testing, by deVries. (Book Review)........ 1176
Spencer, G. L. Electric Oven for Rapid Moisture Tests........ 70
Flask Calibrating and Marking Device........ 1058
Rotary Digester for Use in Bagasse Analysis........ 640
Sperr, F. W., Jr. Benzol, Its Recovery, Rectification, and Uses, by Whitehead. (Book Review)........ 968
and E. H. Bird. By-Product Coking. Fuel Symposium, Chicago Meeting, A. C. S........ 26
Sperry, D. R. Fundamental Laws of Filtration with Suggestions Regarding Research Work. Filtration Symposium, New York Meeting, A. C. S........ 986
Study of the Fundamental Laws of Filtration Using Plant-Scale Equipment. (*See* Baker, 610)........ 1163
Sprague, F. O. Spare Time—A Criticism. (*See* Jordan, 253; Joyce, 651; Dedlow, 1067)........ 474
Springer, J. F. The Feeding of Filters. Filtration Symposium, New York Meeting, A. C. S........ 986
Spry, F. H. and J. M. Bell. Studies on the Nitrotoluenes. VII—The Three-Component System: *p*-Nitrotoluene, *o*-Nitrotoluene, 1,2,4,6-Trinitrotoluene........ 308
J. M. Bell, E. B. Cordon and W. White. Studies on the Nitrotoluenes. V—Binary Systems of *o*-Nitrotoluene and Another Nitrotoluene........ 59
Stacey, A. E., Jr. and W. H. Carrier. Compartment Dryer. Drying Symposium, Rochester Meeting, A. C. S........ 438
Stansfield, E. Carbonization of Canadian Lignite. Fuel Symposium, Chicago Meeting, A. C. S........ 17
Stearn, A. E., H. V. Farr and N. P. Knowlton. An Investigation of the U. S. P. Assay for Phosphoric Acid and Soluble Phosphates.. 220
Stevens, H. P. The Variability of Crude Rubber. (*See* Tuttle, 519)........ 1165
Stevenson, R. and C. Baskerville. Recovering Newsprint........ 213
Stewart, C. R. and L. A. Congdon. A New Qualitative Test for Sucrose in the Presence of Glucose........ 1143
Stratton, S. W. Standardization and Research........ 727
Straub, A. A., A. C. Fieldner and G. W. Jones. Gasoline Losses Due to Incomplete Combustion in Motor Vehicles. Fuel Symposium, Chicago Meeting, A. C. S........ 51
Stuart, E. H. and H. W. Rhodehamel. Atropine Sulfate from *Datura stramonium*........ 218
Sweet, S. and S. E. Sheppard. Setting and Melting Points of Gelatins........ 423

Tanner, F. W. and B. Feuer. The Action of Ultraviolet Rays on the Saccharomycetes. [*See* This Journal, **12** (1920), 740]........ 265
Tartar, H. V. and H. E. Keyes. The Electrical Conductivity of Solutions of Zinc Sulfate in the Presence of Sulfuric Acid........ 1127
Taylor, H. S. The Mechanism of Catalytic Processes........ 75
Taylor, W. C. and A. Bailey. Graded Seal for Joining Pyrex to Lead Glass........ 1158
Teeple, J. E. Address of Welcome. New York Meeting, A. C. S... 866
American Potash Industry and Its Problems........ 249
Thomas, A. W. and M. W. Kelly. Effect of Concentration of Chrome Liquor upon the Adsorption of Its Constituents by Hide Substance........ 65
Tingle, A. Notes on Volumetric Determination of Aluminium in Its Salts. (*Correction*, 655)........ 420
Torossian, G. Action of Anhydrous Stannic Chloride on Petroleum and Its Distillates........ 903
Tour, R. S. Ammonia and the Nitrides, by Maxted. (Book Review)........ 665
Some Interpretations of the Ammonia Synthesis Equilibrium........ 298
Trowbridge C. E. Detection of Phenols in Water (*See* Scott, 422, 574)........ 848
Tschudy, E. A. Effect of Variation in Analytical Constants of Linseed and Soy-Bean Oils upon Quantitative Determination of Linseed Oil in Mixtures of Two Oils by Means of Iodine and Hexabromide Numbers of the Fatty Acids........ 941
Tucker, W. K. Nitrocellulose and Its Solutions as Applied to the Manufacture of Artificial Leather. (*Correction*, 1082)........ 623
Turrentine, J. W. and P. S. Shoaff. Potash from Kelp. IV—Continuous Countercurrent Lixiviation of Charred Kelp........ 605
Tuttle, J. B. Plantation Rubber and Testing of Rubber, by Whitby. (Book Review)........ 967
Variability of Crude Rubber. (*See* Stevens, 1165)........ 519
Twitchell, E. Precipitation of Solid Fatty Acids with Lead Acetate in Alcoholic Solution........ 806

Uyeda, Y. Studies on Bast Fibers. II—Cellulose in Bast Fibers... 141

Vallez, H. A. Vallez Rotary Filter. Filtration Symposium, New York Meeting, A. C. S........ 1007
VanMarle, D. J. and C. O. Lavett. Vacuum Drying. Drying Symposium, Rochester Meeting, A. C. S........ 600
VanWinkle, W. A. Titration Bench........ 146
Veitch, F. P. and T. D. Jarrell. Water Resistance of Treated Canvas during Continuous Exposure to Weather........ 672
Venable, F. P. The Society's President for 1921. E. F. Smith...... 106
Verhulst, J. H., W. H. Peterson and E. B. Fred. Fermentation Process for Production of Acetone, Alcohol, and Volatile Acids from Corncobs........ 757
Volwiler, E. H. Report, Division of Chemistry of Medicinal Products. New York Meeting, A. C. S........ 958
Voress, C. L., G. A. Burrell and G. G. Oberfell. Charcoal Method of Gasoline Recovery. Fuel Symposium, Chicago Meeting, A. C. S. (Note)........ 58
Voris, C. R., O. W. Brown and C. O. Henke. A Dry Method of Preparing Lead Arsenate........ 531

Wadman, W. E. The Determination of "Strength" of Neutralizing Power of Acid Calcium Phosphates........ 1146
Wadsworth, J. W., Jr. Some Problems of National Defense. Address, Rochester Meeting, A. C. S........ 382
Waidner, C. W. and E. F. Mueller. Note on Partial and Total Immersion Thermometers........ 237
Walker, O. J. and G. S. Whitby. Influence of Certain Organic Accelerators on Vulcanization of Rubber........ 816
Walker, P. H. Red Lead and How to Use It in Paint, by Sabin. (Book Review)........ 585
Washburn, E. W. Silica and the Silicates, by Audley. (Book Review)........ 1093
C. W. Parmelee and R. K. Hursh. Selected Bibliography of Books, in the English Language, Dealing with Ceramic Chemistry and the Ceramic Industries........ 476
Waters, C. E. Catalytic Oxidation of Petroleum Oils........ 901
Lubricating and Allied Oils. A Handbook for Chemists, Engineers and Students, by Evans. (Book Review)........ 1091
Weidlein, E. R. Report of the Representative of the A. C. S. on the Joint Committee Supervising the Publication of the Chemical Engineering Catalog for the Year 1920........ 569
Wells, R. C. Alkalinity of Searles Lake Brine........ 691
Wells, S. D. Chemical Constitution of Soda and Sulfate Pulps from Coniferous Woods and Their Bleaching Qualities........ 936
Wendt, G. L. Science and Life, by Soddy. (Book Review)........ 274
Whitaker, M. C. Industrial Alcohol and Its Relation to Prohibition Enforcement from Manufacturer's Standpoint........ 647
Whitby, G. S. and O. J. Walker. Influence of Certain Organic Accelerators on Vulcanization of Rubber........ 816
White, W., J. M. Bell, E. B. Cordon and F. H. Spry. Studies on the Nitrotoluenes. V—Binary Systems of *o*-Nitrotoluene and Another Nitrotoluene........ 59
Whitescarver, W. F. and R. D. Bonney. The Direct Identification of Soy-Bean Oil. [*See* This Journal, **12** (1920), 1174]........ 574
Whitney, W. R. Acceptance Address: Biggest Things in Chemistry. Perkin Medal Award........ 161
Wichmann, H. J. A New Lead Number Determination in Vanilla Extracts........ 414
Wiegand, W. B. Rubber Energy........ 118
Rubber Manufacture, by Simmons. (Book Review)........ 663
Wiley, J. A. and G. L. Kelley. Determination of Chromium in Ferrochromium by Electrometric Titration........ 1053
G. L. Kelley, R. T. Bohn and W. C. Wright. Determination of Vanadium and Chromium in Ferrovanadium by Electrometric Titration........ 939
Will, E. G. and R. D. Scott. Cider Preservatives........ 1141
Williams, R. R. Vitamines from the Standpoint of Structural Chemistry. Vitamine Symposium, New York Meeting, A. C. S... 1107
Wilson, C. P. The Manufacture of Citric Acid from Lemons........ 554
Wilson, J. A. Report of the Division of Leather Chemistry. New York Meeting, A. C. S........ 958
and G. Daub. Critical Study of Bating........ 1137
and H. M. Heisig. Role of Acidity in Dehydration of Sewage Sludge........ 406
and E. J. Kern. Color Value of a Tan Liquor as a Function of the Hydrogen-Ion Concentration........ 1025
Determination of Tannin........ 772
Wilson, O. G., Jr. and L. W. Parsons. Some Factors Affecting the Stability and Inversion of Oil-Water Emulsions. Emulsification Symposium, New York Meeting, A. C. S........ 1116
Wilson, R. E. Humidity Control by Means of Sulfuric Acid Solutions, with Critical Compilation of Vapor Pressure Data........ 326
and D. P. Barnard, 4th. Condensation Temperatures of Gasoline- and Kerosene-Air Mixtures........ 906
Total Sensible Heats of Motor Fuels and Their Mixtures with Air........ 912
W. G. Horsch and M. A. Youtz. Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese. (*Correction*, 960)........ 763
Winter, O. B., C. S. Robinson and E. J. Miller. Studies of Availability of Organic Nitrogenous Compounds—I........ 933
Withrow, J. R. Chemists' Year Book, 1920, by Atack and Winyates. (Book Review)........ 100
Condensed Description of the Manufacture of Beet Sugar, by Murke. (Book Review)........ 664

WITTEVEEN, H. J. AND E. F. FARNAU. Colors Developed by Cobalt Oxides.......... 1061
WOLCOTT, E. R. New Crystalline Form of Potassium Chlorate...... 215
WOOD, J. T. Properties and Action of Enzymes in Relation to Leather Manufacture.......... 1135
WRIGHT, A. Industrial Filter Media. Filtration Symposium, New York Meeting, A. C. S.......... 984
WRIGHT, A. H. AND P. GROSS. Distillation Apparatus.......... 701
WRIGHT, W. C., G. L. KELLEY, J. A. WILEY AND R. T. BOHN. Determination of Vanadium and Chromium in Ferrovanadium by Electrometric Titration.......... 939

YANCEY, H. F. AND T. FRASER. The Distribution of the Forms of Sulfur in the Coal Bed. Fuel Symposium, Chicago Meeting, A. C. S.......... 35
YOUTZ, M. A., R. E. WILSON AND W. G. HORSCH. Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese. (*Correction*, 960).......... 763

ZANETTI, J. E. French-English Dictionary for Chemists, by Patterson. (Book Review).......... 1177
  AND M. KANDELL. Formation of Anthracene from Benzene and Ethylene. (*Correction*, 358).......... 208
ZELLER, S. M. AND H. SCHMITZ. Toxicity of Various Fractions and Combinations of Fractions of Coal-Tar Cresote to Wood-Destroying Fungi.......... 621
ZOLLER, H. F. Precipitation of Grain-Curd Casein from Pasteurized Milk, Including Sweet Cream Buttermilk.......... 510
  AND Y. OKUDA. The Relations of Hydrogen-Ion Concentration to the Heat Coagulation of Proteins in Swiss Cheese Whey.......... 515

SUBJECT INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY
VOLUME XIII—1921

- ABRASIVE Materials, by Beach and Coons, in 1919, 1088, Tariff Information Surveys. Gov. Pub. 742
- Accelerators, Organic, Action of Certain—in Vulcanization of Rubber. [*See* THIS JOURNAL, **12** (1920), 317] G. D. Kratz, A. H. Flower and B. J. Shapiro. II, 67; III 128
- Accelerators, Organic, Influence of Certain—on Vulcanization of Rubber. G. S. Whitby and O. J. Walker 816
- Accelerators, Reactions of—during Vulcanization: [*See* THIS JOURNAL, **12** (1920), 31]
  - II—Theory of Accelerators Based on Formation of Polysulfides during Vulcanization. W. Scott and C. W. Bedford 125
  - III—Carbo-Sulfhydryl Accelerators and Action of Zinc Oxide. C. W. Bedford and L. B. Sebrell 1034
- Acenaphthene, Chemistry of—and Its Derivatives. D. A. Hahn and H. E. Holmes 822
- Acetone, Alcohol and Volatile Acids, Fermentation Process for Production of—from Corncobs. W. H. Peterson, E. B. Fred and J. H. Verhulst 757
- Acetylene, Preparation of Ethylene by Hydrogenation of. W. H. Ross, J. B. Culbertson and J. P. Parsons 775
- Acids:
  - Acetic and Lactic, Fermentation Process for Production of—from Corncobs. E. B. Fred and W. H. Peterson 211
  - Benzenedisulfonic, from Benzenemonosulfonic Acid. C. E. Senseman 1124
  - Citric, Manufacture of—from Lemons. C. P. Wilson 554
  - Hydrocyanic, Fumigation of Citrus Plants with. Woglum. Gov. Pub 97
  - Hydrocyanic, in Sudan Grass. Swanson. Gov. Pub 1175
  - Maleic and Fumaric, Applications of—and Their Salts in Textile Industry. J. H. Carpenter 410
  - Maleic and Malic, Production of Coumarins from. G. C. Bailey and F. Boettner 905
  - Nitroglycerin Spent, Use of—as Charging Acid for Nitric Acid Stills. S. G. Norton 677
  - Orthophosphoric, Revised Specific Gravity Table for—at 25°/25° C. N. P. Knowlton and H. C. Mounce 1157
  - β-Oxynaphthoic and J-, Dyes Derived from—, with Reference to Chemical Foundation Patents. A. W. Joyce 946
  - β-Oxynaphthoic, Anilides of. E. R. Brunskill 309
  - Perchloric, Use of—as Aid to Digestion in Kjeldahl Nitrogen Determination. B. Mears and R. E. Hussey 1054
  - Phosphoric, Investigation of U. S. P. Assay for—and Soluble Phosphates. A. E. Stearn, H. V. Farr and N. P. Knowlton 220
  - Reagent Chemicals. I—Proposed Specification for Sulfuric, Nitric, and Hydrochloric Acids, and for Ammonium Hydroxide. W. D. Collins 735
  - Solid Fatty, Precipitation of—with Lead Acetate in Alcoholic Solution. E. Twitchell 806
  - Sulfuric, Electrical Conductivity of Solutions of Zinc Sulfate in Presence of. H. V. Tartar and H. E. Keyes 1127
  - Tariff Information Surveys. Gov. Pub 659, 742
  - Volatile, Fermentation Process for Production of Acetone, Alcohol, and—from Corncobs. W. H. Peterson, E. B. Fred and J. H. Verhulst 757
- ADDRESSES AND CONTRIBUTED ARTICLES 72, 147, 247, 334, 460, 564, 641, 714, 822, 946, 1059
- Aeronautics. Gov. Pub.:
  - Aviation Gasoline, Specifications and Methods of Testing 97
  - Comparison of Alcogas Aviation Fuel with Export Aviation Gasoline. Gage, *et al* 97
  - Comparison of Hector Fuel with Export Aviation Gasoline. Dickinson, *et al* 97
  - Fifth Annual Report of National Advisory Committee for—, 1919 175
- Agricultural and Food Chemistry, Division of. Report, New York Meeting, A. C. S. T. J. Bryan 958
- AGRICULTURAL AND INDUSTRIAL CHEMISTRY IN BRITISH WEST INDIES, WITH SOME ACCOUNT OF WORK OF SIR FRANCIS WATTS. C. A. Browne 78
- Air, Liquid, on Laboratory Scale. Cook. Gov. Pub 1089
- Airplane Dopes: European Practice in Cellulose Acetate and Dopes during War. P. Drinker 831
- Airplanes, Preventing Corrosion of Metal Parts of. Gov. Pub 964
- Alaska Mining Experiment Station. Davis. Gov. Pub 492
- Alaska Mining, Future of—, and—Industry in 1919. Brooks and Martin. Gov. Pub 369
- ALCOHOL:
  - *Addresses and Original Papers:*
    - Alcohol and Chemical Industries. J. M. Doran 564
    - Fermentation Process for Production of Acetone,—and Volatile Acids from Corncobs. W. H. Peterson, E. B. Fred and J. H. Verhulst 757
    - Forests of U. S. as a Source of Liquid Fuel Supply. R. C. Hawley. 1059
    - Industrial, Its Relation to Prohibition Enforcement from Manufacturer's Standpoint. M. C. Whitaker 647
    - Motor Fuel from Vegetation. T. A. Boyd 836
    - Rapid Volumetric Method for Determining. A. Lachman 230
    - Role of Chemist in Relation to Future Supply of Liquid Fuel. H. Hibbert 841
  - *Editorials:*
    - Alcoholic Tribulations 591
    - Editorial Note 975
    - Less Legislation—More Coöperation 503
    - Vicarious Punishment 187
    - When a Law Defeats Itself—Repeal It! 3
  - *Government Publications:*
    - Denatured Alcohol 369
    - Test for Determining Quality of Milk for Condenseries. Dahlberg and Garner 660
  - *Notes:*
    - Alcohol-Water Mixtures, Vapor Composition of. P. N. Evans and W. K. Lewis. [*See* THIS JOURNAL, **12** (1920), 296] 168
    - Industrial, Local Sections Protest against—Restrictions. Joint Meeting, June 10, 1921 651
- Alkali Fusions. [*See* THIS JOURNAL, **12** (1920), 145, 857, 1028]
  - III—Fusion of Phenylglycine-*o*-Carboxylic Acid for Production of Indigo. M. Phillips 759
- Alkalinity of Searles Lake Brine. R. C. Wells 691
- Alkylation of Aromatic Amines by Heating with Aliphatic Alcohols. A. J. Hill and J. J. Donleavy 504
- Alloys, White Metal-Bearing, Properties of—at Elevated Temperatures. Freeman and Woodward. Gov. Pub 581
- Alsace: Alsatian Potash Industry. Note 227
- Aluminates, Calcium, Cementing Qualities of. Bates. Gov. Pub 1089
- Aluminium and Bauxite in 1920. Hill. Gov. Pub 1088
- Aluminium Compounds. Tariff Information Surveys. Gov. Pub 659
- Aluminium, Metallic, Determination of—and of Aluminium Oxide in Commercial Metal. J. H. Capps 808
- Aluminium, Notes on Volumetric Determination of—in Its Salts. A. Tingle. (*Correction*, 655) 420
- AMERICAN CERAMIC SOCIETY:
  - 24th Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922. Announcement 684
  - Conference, New York City, September 15, 1921. Report 891
- American Chemical Industry and Its Need for Encouragement and Protection. Address, Rochester Meeting, A. C. S. N. Longworth 384
- AMERICAN CHEMICAL SOCIETY:
  - Corporation Members: Are Your Folks on the List? Editorial, 3; List 91
  - Edgar Fahs Smith, Society's President for 1921. F. P. Venable 106
  - *60th (Annual) Meeting, Chicago, Ill., September 6 to 10, 1920:*
  - FUEL SYMPOSIUM:
    - Low-Temperature Carbonization and Its Application to High Oxygen Coals. S. W. Parr and T. E. Layng. (*Correction*, 266) 14
    - Carbonization of Canadian Lignite. E. Stansfield 17
    - Commercial Realization of Low-Temperature Carbonization of Coal. H. A. Curtis 23
    - By-Product Coking. F. W. Sperr, Jr. and E. H. Bird 26
    - By-Product Coke, Anthracite, and Pittsburgh Coal as Fuel for Heating Houses. H. Kreisinger 31
    - Some Factors Affecting Sulfur Content of Coke and Gas in Carbonization of Coal. A. R. Powell 33
    - Distribution of Forms of Sulfur in Coal Bed. H. F. Yancey and T. Fraser 35
    - Colloidal Fuels, Their Preparation and Properties. S. E. Sheppard 37
    - Fuel Conservation, Present and Future. H. C. Porter 47
    - Gasoline Losses Due to Incomplete Combustion in Motor Vehicles. A. C. Fieldner, A. A. Straub and G. W. Jones 51
    - Enrichment of Artificial Gas with Natural Gas. J. B. Garner 58
    - Charcoal Method of Gasoline Recovery. G. A. Burrell, G. G. Oberfell and C. L. Voress. Note 58
  - *61st Meeting, Rochester, N. Y., April 26 to 29, 1921:*
    - An Anomaly. Editorial 378
    - Convention Side Lights 404
    - Council Meeting 378
    - Division and Section Meetings 398
    - Dye Chemists. Note 354
    - Editorial Note 5
    - On to Rochester! Editorial 282
    - Petroleum Section, Initial Meeting 353
    - Plans for the Spring Meeting. Announcement 166
    - Preliminary Program 266
    - Program 480
    - Rochester Ready for Chemical Cohorts. J. W. Harrington 352
    - Section of Historical Chemistry 397
    - Story of the Week 380
    - Symposium on Drying. Note 267
  - ADDRESSES:
    - Address of Welcome. E. G. Miner 380
    - American Chemical Industry and Its Need for Encouragement and Protection. N. Longworth 384
    - Chemistry in the United States. C. F. Chandler 391
    - Place of Chemistry in Business. A. D. Little 386
    - Some Problems of National Defense. J. W. Wadsworth, Jr. 382
  - SYMPOSIUM ON DRYING:
    - Rate of Drying of Solid Materials. W. K. Lewis 427
    - Theory of Atmospheric Evaporation—with Special Reference to Compartment Dryers. W. H. Carrier 432
    - Compartment Dryer. W. H. Carrier and A. E. Stacey, Jr. 438
    - Spray Process of Drying. R. S. Fleming 447
    - Direct Heat Rotary Drying Apparatus. R. G. Merz 449
    - Tunnel Dryers. G. B. Ridley 453
    - Vacuum Drying. C. O. Lavett and D. J. Van Marle 600
  - *62nd (Annual) Meeting, New York, N. Y., September 6 to 10, 1921:*
    - A Time for Gathering. Editorial 670
    - Chairmen of Local Committees 734
    - Chemistry's Greatest Rally. J. W. Harrington 733
    - Council Meeting 865
    - Englishman's Impression of the N. Y. Meeting 1170
    - From the Tower. Editorial 865
    - General Meeting 866
    - Hotel Accommodations. Announcement. C. F. Lindsay 571
    - International Meeting 881
    - Meeting of Section of Chemical Education. J. C. Olsen 1074
    - Message of Welcome and Call to Duty. E. F. Smith 844
    - Plant Excursions. Note. J. V. N. Dorr 1170

Program of Meetings 845
Program of Papers 951
Public Meeting 879
Reduced Railroad Rates 734
Reports of Meetings of Divisions and Sections 956
Resolutions on Organic Chemical Industry 873
Side Lights 885
Symposium on Chemistry in Coking and Gas Industries. Note 706
Symposiums and Special Orders in Divisional Meetings 878
The Meeting and the Exposition Editorial 752
Welcome to Our Visitors. Editorial 750
ADDRESSES:
Address of Welcome. J. E. Teeple 866
Chemistry and the State. F. P. Garvan 866
Modern Developments in War Making. W. J. Pope 874
Plan for Development of Industrial Research in Canada. R. F. Ruttan 876
Priestley: Presentation of Portrait. C. A. Browne 879
EMULSIFICATION SYMPOSIUM
Emulsions with Finely Divided Solids. T. R. Briggs 1008
Emulsifying Agents in Oil-Field Emulsions. J. L. Sherrick 1010
Common Characteristics of Crude Petroleum Emulsions. E. E. Ayres, Jr. 1011
Oil-Field Practice in Handling Crude Oil Emulsion. S. Born 1013
Recovering Petroleum from Emulsions by Chemical Treatment. R. R. Matthews and P. A. Crosby 1015
Discussion of Electrical Dehydration of Crude Oil. W. G. and H. C. Eddy 1016
Some Factors Affecting Stability and Inversion of Oil-Water Emulsions. L. W. Parsons and O. G. Wilson, Jr. 1116
FILTRATION SYMPOSIUM:
Washing and Washing Ports in Connection with "Chamber" and "Frame" Filter Presses. E. A. Alliott. 976
Filter Cloth and Its Relation to Filtration. A. A. Campbell 982
Industrial Filter Media. A. Wright 984
Feeding of Filters. J. F. Springer 986
Fundamental Laws of Filtration with Suggestions Regarding Research Work. D. R. Sperry 986
Filter Aids. C. P. Derleth 989
Use of Filter-Cel for Industrial Filtration Processes. G. M. Hickey 990
Centrifugal Filters. H. C. Beckman 992
Centrifugal Draining. T. A. Bryson 993
Pulp or Filter Mass Filters. E. E. Finch 996
Leaf and Rotary Suction Filters. G. D. Dickey 997
Plate and Frame Filter Presses. G. B. Rice 1000
Modern Leaf Type Filters. R. C. Campbell 1002
Oliver Continuous Filters. H. A. Morrison 1005
Atkins-Shriver Automatic Filter Press. H. D. Atkins 1006
Vallez Rotary Filter. H. A. Vallez 1007
VITAMINE SYMPOSIUM:
Factors Influencing Vitamine Content of Foods. R. A. Dutcher 1102
Standardized Feeding Methods for Study of Vitamines. A. D. Emmett 1104
Vitamines from Standpoint of Structural Chemistry. R. R. Williams 1107
Vitamines from Standpoint of Physical Chemistry. V. K. LaMer. 1108
Antiberiberi Vitamine. C. Funk 1110
Experiments on Isolation of Antineuritic Vitamine. A. Seidell 1111
Antiscorbutic Vitamine. A. F. Hess 1115
A. C. S. News Service:
Appreciations. Editorial 188
Expansion of the News Service. Editorial 4
Editorials:
Every Man's Job 975
Committees:
Adoption by Colleges of Standard Metric Units. E. C. Bingham. 1068
Delegate to Conference Called by the American Petroleum Institute, N. Y., April 11, 1921. Report. T. G. Delbridge 403
Editorial Note 405
Guaranteed Reagents and Standard Apparatus. Report. W. D. Collins 402, 1070
Industrial Alcohol. Report 570
Institute for Chemo-Medical Research. Report. C. H. Herty 404
Metric System. Report. E. C. Bingham 401
Occupational Diseases in Chemical Trades. Report. C. Baskerville 568
Representative of A. C. S. on Joint Committee Supervising Publication of Chemical Engineering Catalog for Year 1920. Report. E. R. Weidlein 569
To Coöperate with Chemical Warfare Service. Report. C. H. Herty 403
Divisions and Sections:
Cellulose Section. Announcement 166
Industrial and Engineering Chemistry—Submittal of Papers. H. E. Howe 570
Local Sections:
Cincinnati. Dr. Martin Fischer Tells of European Trip 345
Editorial Note 975
Meetings, 1921–22 1079, 1169
Milwaukee. No Time for Dullness. Editorial 4
New York. Joint Meeting with Other Chemical Societies. New York City, February 11, 1921. Note 167
Monographs:
"Glue and Gelatin." Note 632
Thoughts Translated into Deeds. Editorial 108
Secretary's Office:
Advisory Committee Resolution on C. W. S. Note 266
Honorary Members. Letters of Acceptance, W. J. Pope and P. Kestner 1170
Membership Directory of the Society. Note 737
Officers for 1921 2
AMERICAN DRUG MANUFACTURERS' ASSOCIATION:
10th Annual Meeting, New York, N. Y., April 11 to 14, 1921 485
AMERICAN ELECTROCHEMICAL SOCIETY:
39th Meeting, Atlantic City, N. J., April 21 to 23, 1921. Report. J. W. Richards 483
40th Meeting, Lake Placid, September 29 to October 1, 1921. Report. J. W. Richards 1076
New York Section. Joint Meeting. February 11, 1921. Note 167
Research. Address. E. F. Smith 254
AMERICAN INSTITUTE OF BAKING:
Malt Extracts and Shortening Agents Registered by 1028
Research Fellowships. Note 92
AMERICAN INSTITUTE OF CHEMICAL ENGINEERS:
13th Annual Meeting, New Orleans, La., December 6 to 9, 1920. Report J. C. Olsen 89
13th Semiannual Meeting, Detroit, Michigan, June 20 to 25, 1921. Announcement, 563; Report. J. C. Olsen 652
Banquet, New York City, September 14, 1921 891
AMERICAN OIL CHEMISTS' SOCIETY 331
Coöperative Analytical Work. F. N. Smalley 655
AMERICAN PHARMACEUTICAL ASSOCIATION. Note 632
American Railway Development Association. The Chemist and the Railways. Editorial 591
Amesite and Corundophilite, Chester, Mass. Shannon. Gov. Pub 175
Amines, Aromatic, Alkylation of—by Heating with Aliphatic Alcohols. A. J. Hill and J. J. Donleavy 504
Ammonia:
Absorption Refrigerator Machines, Noncondensable Gases in. McKelvy and Isaacs. Gov. Pub 272
Synthesis, Some Interpretations of—Equilibrium. R. S. Tour 298
Ammonium Compounds. Tariff Information Surveys. Gov. Pub 659
Ammonium Hydroxide, Proposed Specification for Sulfuric, Nitric, and Hydrochloric Acids, and for. Reagent Chemicals, I. W. D. Collins. 735
Ammonium Sulfate, Effect of—upon Plants in Nutrient Solutions Supplied with Ferric Phosphate and Ferrous Sulfate. Jones and Shive. Gov Pub 1174
Ammonium Sulfate, Melting Point of. J. Kendall and A. W. Davidson. 303
Ampère: Centenary of Founding of Sciences of Electromagnetism and Electrodynamics. C. A. Doremus 166
Annatto, Test for—in Fats and Oils. W. Brinsmaid 216
Annual Tables of Constants. (*Correction*, 480), 313; Note 509
Anthracene, Formation of—from Benzene and Ethylene. J. E. Zanetti and M. Kandell. (*Correction*, 358) 208
Anthracite, By-Product Coke, and Pittsburgh Coal as Fuel for Heating Houses. H. Kreisinger 31
Antimony in 1919, 743; in 1920. Schrader. Gov. Pub 1174
APPARATUS (*See under name of piece*)
Apparatus, Duty-Free. Aftermath. Editorial. [*See* THIS JOURNAL, **12** (1920), 1146] 187
Apparatus, Duty-Free. Elementary Economics. Editorial 107
Apparatus, Industrial Laboratory, Standardization of. Note 92
Apparatus, Report on Standardization of Sizes and Shapes of—, I. W. D. Collins 1070
Arsenate, Lead, Dry Method of Preparing. O. W. Brown, C. R. Voris and C. O. Henke 531
Arsenate, Tricalcium, Preparation and Instability of. J. H. Reedy and I. L. Haag 1038
Arsenic Compounds, Quantitative Pathological Studies with. Hooper, *et al.* Gov. Pub 964
Arsenic in 1920. Heickes. Gov. Pub 1088
Arsphenamine, Effect of Shaking—in Air. Roth. Gov. Pub 175
Asbestos in 1919. Diller. Gov. Pub 660
Asphalt. Tariff Information Surveys. Gov. Pub 742
Asphalt and Related Bitumens in 1919, 964; in 1920. Cottrell. Gov. Pub 1088
Assignment of Patents. (*See* Merchant, 849) 646
ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS:
37th Annual Convention, Washington, D. C., November 15 to 17, 1920 90
38th Annual Convention, Washington, D. C., October 24 to 26, 1921. Announcement, 943; Report. N. A. Parkinson 1168
ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS:
Meeting, New York City, September 13, 1921 891
Meeting, Boston, Mass, November 3, 1921 1162
Atropine Sulfate from *Datura stramonium*. H. W. Rhodehamel and E. H. Stuart 218
Autoclave, Combined Extractor, Reflux Condenser, Still and. A. T. Shohl and M. L. Koch 819
Autoclave, Large-Capacity. A. B. Andrews 560

BAGASSE, Rotary Digester for Use in—Analysis. G. L. Spencer 640
Bags, Paper, Developing Standard Specifications for—for Cement and Lime. Houston. Gov. Pub 581
Bakelite Company Wins Decree 769
Bakelite: Further Studies on Phenolic Hexamethylenetetramine Compounds. M. Harvey and L. H. Baekeland 135
Baking Powder:
Determination of "Strength" or Neutralizing Power of Acid Calcium Phosphates. W. E. Wadman 1146
Balsams. Tariff Information Surveys. Gov. Pub 659
Barium Carbonate, Toxicity of—to Rats. Schwartze. Gov. Pub 98
Barytes. Tariff Information Surveys. Gov. Pub 659
Barytes and Barium Products in 1919. Stone. Gov. Pub 854
Bast Fibers, Studies on. [*See* THIS JOURNAL, **12** (1920), 573] II—Cellulose in Bast Fibers. Y. Uyeda 141
Bath, Constant-Temperature, for Heating Blood Serum. Henley. Gov. Pub 965
Bating, Critical Study of. J. A. Wilson and G. Daub 1137
Bauxite and Aluminium in 1920. Hill. Gov. Pub 1088
Bean Seedlings, Utilization of Mineral Constituents. Buckner. Gov. Pub 492
Beets, Sugar, Process for Producing Palatable Sirup from. S. F. Sherwood 799
Belgian Bureau of Chemical Standards. Note 539
Belgium and France, Industrial Machinery in. (With Bibliography) Wood. Gov. Pub 177
Benzenedisulfonic Acid from Benzenemonosulfonic Acid. C. E. Senseman 1124
Benzyl Succinate: Preliminary Report on Composition, Manufacture, Properties, and Probable Therapeutic Uses. M. Bye 217
Beta-Oxynaphthoic Acid, Dyes Derived from—and from J-Acid, with Reference to Chemical Foundation Patents. A. W. Joyce 946
BIBLIOGRAPHY, SELECTED—OF BOOKS, IN ENGLISH LANGUAGE, DEALING WITH CERAMIC CHEMISTRY AND CERAMIC INDUSTRIES. E. W. Washburn, C. W. Parmelee and R. K. Hursh 476
Biological Chemistry, Division of. Report, New York Meeting, A. C. S. H. B Lewis 958
Biology: Standardization of Biological Stains 1158
Biscuit and Cracker Manufacturers Association. Passing of Secrecy. Editorial 751
Bismuth. Tariff Information Surveys. Gov. Pub 659, 742
Bismuth in 1920. Heickes. Gov. Pub 1088

Bitumens and Asphalt in 1920. Cottrell. Gov. Pub 1088
Blacking. Tariff Information Surveys. Gov. Pub 659
Bleach Liquor, Apparatus for Rapid Determination of Available Chlorine in. M. Schrero 559
Bloede and Hoffmann Scholarships of Chemists' Club. Note 480
Boiler Water Treatment. Gov. Pub 491
Boll-Weevil, Crop Protection Institute Discusses War on 89
Book Reviews. (*See separate heading*)
Bookstock, Regenerating. C. Baskerville and C. M. Joyce 214
Boron. Gov. Pub 490
Boron in Relation to Fertilizer Industry. J. E. Breckenridge 324
Botulism. Gov. Pub.:
  At St. Anthony's Hospital, Oakland, Cal 97
  Direct Inoculation Test for *B. Botulinus* Toxin. Bengston 1174
  Distribution of Spores of *B. Botulinus* in Nature. Meyer and Geiger 271, 580
  Human, Bacteriological Diagnosis of. Meyer and Geiger 1087
  Spoiled Canned Food and 580
Brass, Determination of Small Amounts of Lead in. F. W. Glaze 553
Brick, Sand-Lime, Description and Specification. Gov. Pub 492
Brick, Sand-Lime, in 1919, 490; in 1920. Middleton. Gov. Pub 1088
Briggs, T. L. Obituary. A. H. Sabin 489
Brine, Searles Lake, Alkalinity of. R. C. Wells 691
British Dyestuffs Committee 313
British Mission, Report of—Appointed to Visit Enemy Chemical Factories in Occupied Zone Engaged in Production of Munitions of War. Specific Facts. Editorial 283
British West Indies, Industrial and Agricultural Chemistry in—with Some Account of Work of Sir Francis Watts. C. A. Browne 78
Bromine in 1919. Insley. Gov. Pub 490
Bromine, Salt and Calcium Chloride in 1920. Stone. Gov. Pub 965
Buchu Leaves. Tariff Information Surveys. Gov. Pub 659
Buffer Action of Water Extracts. Studies of Wheat Flour Grades, II. C. H. Bailey and A. C. Peterson 916
Bumstead, Dr H. A. Note 167
Bureau of Chemistry:
  Organization, Enforcement of Food and Drugs Act, Enforcement of Tea Act, Research Work. Gov. Pub 177
  Report of Chemist, June 1920. Alsberg. Gov. Pub 98
Bureau of Foreign and Domestic Commerce. Gov. Pub 97, 177, 743
Bureau of Internal Revenue. Gov. Pub 369
Bureau of Mines: Director's Annual Report. Gov. Pub 177
  Government Publications 97, 177, 271, 370, 491, 580, 660, 743, 854, 965, 1089
Bureau of Standards:
  Director's Annual Report. Gov. Pub 370
  Government Publications 97, 177, 272, 370, 492, 581, 660, 743, 1089
  War Work of. Gov. Pub 581
Buret and Holder, Improved. C. C. Kiplinger 713
Burners, Atmospheric Gas, Design of. Berry, *et al.* Gov. Pub 1089

Book Reviews 99, 179, 274, 372, 494, 583, 662, 745, 856, 967, 1091, 1176
American Chemistry, by Hale. R. E. Rose 857
American Lubricants, by Lockhart. C. K. Francis 496
Ammonia and Nitrides, by Maxted. R. S. Tour 665
Analysis of Paint Vehicles, Japans, and Varnishes, by Holley. A. H. Sabin 101
Annual Reports of the Society of Chemical Industry on Progress of Applied Chemistry. H. E. Howe 1091
Application of Dyestuffs, by Matthews. W. D. Livermore 99
Applied Colloid Chemistry—General Theory, by Bancroft. G. H. A. Clowes 967
Benzol, Its Recovery, Rectification, and Uses, by Whitehead. F. W. Sperr, Jr 968
Ceramics. A Manual for Chemists, Engineers, and Manufacturers, by Malinovsky. A. V. Bleininger 969
Chemistry and Civilization, by Cushman. W. D. Bancroft 494
Chemistry and Technology of Diazo-Compounds, by Cain. R. E. Rose 583
Chemistry of Enzyme Actions, by Falk. H. T. Graber 372
Chemistry of Pulp and Paper Making, by Sutermeister. H. H. Hanson 583
Chemists' Year Book, 1920, by Atack and Winyates. J. R. Withrow 100
Chimie et la Guerre, by Moureu. A. A. Fries 1092
Chronology of Iron and Steel, *compiled* by Goodale, and *edited* by Speer. G M. Berry 745
Cocoa and Chocolate: Their Chemistry and Manufacture, by Whymper. L. Davis 1093
Condensed Description of Manufacture of Beet Sugar by Murke. J. R. Withrow 664
Copper Refining, by Addicks. J. H. Ransom 857
Determination of Hydrogen Ions, by Clark. R. A. Gortner 372
Dictionary of Applied Chemistry, Vol. I, by Thorpe. A. Rogers 664
Dictionary of Chemical Solubilities: Inorganic, by Comey and Hahn. V. Lenher 662
Dictionary of Chemical Terms, by Couch. A. M. Patterson 583
Estate Rubber: Its Preparation, Properties and Testing, by de Vries. D. Spence 1176
Éthers Cellulosiques; Première Partie, Éthers Minéraux de Cellulose, by Dubosc. G. J. Esselen, Jr 584
Factory Chemistry, by Hawkes. W. D. Bancroft 663
French-English Dictionary for Chemists, by Patterson. J. E. Zanetti. 1177
Fuel Oil in Industry, by Andros. G. A. Burrell 101
Fuel Production and Utilization, by Taylor and *edited* by Rideal. A. C. Fieldner 494
Gas Warfare, by Farrow. B. C. Goss 495
Gasoline and Other Motor Fuels. E. W. Dean 665
Industrial Gases, by Greenwood. H. C. Gillette 181
Industrial Organic Analysis, by Arup. S. P. Sadtler 276
Introduction to Chemical Pharmacology, by McGuigan. A. S. Loevenhart 585
Laboratory Manual for Detection of Poisons and Powerful Drugs, by Autenreith. G. H. Meeker 663
Labor's Crisis, by Mendelsohn. H. W. Jordan 665
Lubricating and Allied Oils, A Handbook for Chemists, Engineers and Students, by Evans. C. E. Waters 1091
Manufacture of Chemicals by Electrolysis, by Hale. C. G. Fink 274
Manufacture of Sugar from the Cane and the Beet, by Heriot. W. D. Horne 277
Margarine, by Clayton. C. Baskerville 181
Metallography, Part II. The Metals and Common Alloys, by Hoyt. H. Fay 856
Microbiology and Microanalysis of Foods, by Schneider. E. M. Chamot 100
Modern Electroplater, by Coggeshall. W. Blum 179
Natural Organic Colouring Matters, by Perkin and Everest. E. S. Chapin 274
Nature of Animal Light, by Harvey. G. M. J. Mackay 180
New Stone Age, by Howe. C. F. Binns 584
Official and Tentative Methods of Analysis of Association of Official Agricultural Chemists, *compiled* by Doolittle, *et al.* 496
Papers on Paint and Varnish, by Gardner. E. F. Ladd 497
Plantation Rubber and Testing of Rubber, by Whitby. J. B. Tuttle 967
Rapid Methods for Chemical Analysis of Special Steels, Steel Making Alloys, Their Ores, and Graphites, by Johnson. A. A. Blair 497
Red Lead and How to Use It in Paint, by Sabin. P. H. Walker 585
Rubber Manufacture, by Simmons. W. B. Wiegand 663
Rubber, Resins, Paints and Varnishes, by Morrell and de Waele. A. H. Gill 856
Science and Life, by Soddy. G. L. Wendt 274
Silica and Silicates, by Audley. E. W. Washburn 1093
Simple Carbohydrates and the Glucosides, by Armstrong. C. S. Hudson 276
Soil Alkali, by Harris. R. O. E. Davis 179
Tables of Refractive Indices. II—Oils, Fats and Waxes, *compiled* by Kanthack and *edited* by Goldsmith. G. H. Pickard 1092
Technical Examination of Crude Petroleum, Petroleum Products and Natural Gas, by Hamor and Padgett. G. W. Gray 662
Technical Gas and Fuel Analysis, by White. A. C. Fieldner 180
Technical Methods of Analysis, *edited* by Griffin. P. C. McIlhiney 745
Technical Records of Explosives Supply. 1915–1918. I—Denitration of Spent Acids. II—Manufacture of Trinitrotoluene (TNT). C. E. Munroe 1176
Textbook of Chemical Engineering, by Hart. R. T. Haslam 495
Traité de la Conservation et de l'Amelioration des Bois, by de Keghel. C. J. Humphrey 969
Unification des Noms des Colorants les Plus Usuels, by Sisley. C. G. Derick 497
Vernis, by Coffignier. C. R. Bragdon 745
Vitamines—Essential Food Factors, by Harrow. A. Seidell 584

CADMIUM in 1920. Siebenthal and Stoll. Gov. Pub 660
Cal, Effects of—as Accelerator of Hardening of Portland Cement. Young. Gov. Pub 177
Calcium:
  Aluminates, Cementing Qualities of. Bates. Gov. Pub 1089
  Chloride, Bromine and Salt in 1920. Stone. Gov. Pub 965
  Chloride in 1919. Insley. Gov. Pub 490
  Chloride Method for Determination of Water in Gasoline and in Certain Other Substances. C. W. Clifford 628
  Chloride, Solubility of Water in Gasoline and in Certain Other Organic Liquids, Determined by—Method. C. W. Clifford 631
  Content, Relation of—of Some Kansas Soils to Soil Reaction as Determined by Electrometric Titration. Swanson, *et al.* Gov. Pub. 492
  Influence of Phosphorus and—in the Feed on Milk Yield. Meigs and Woodward. Gov. Pub 661
Calendar of Meetings 90, 167, 267, 358, 485, 572, 654, 737, 846, 960, 1079, 1169
Calibrating and Marking Device. G. L. Spencer 1058
Camphor Substitutes in Manufacture of Celluloid. A. P. Sachs and O. Byron 893
Canada, Plan for Development of Industrial Research in. Address, New York Meeting, A. C. S. R. F. Ruttan 876
Cane-Sirup Canning, Coöperative. Dale. Gov. Pub 98
Canvas, Treated, Water Resistance of—during Continuous Exposure to Weather. F. P. Veitch and T. D. Jarrell 672
Carbon:
  Dioxide Content of Barn Air. Hendry and Johnson. Gov. Pub 370
  Dioxide, Free and Combined, Method for Determination of. J. A. Shaw 1151
  Dioxide, Solid Sodium Hydroxide as Absorbent for—in Steel Analysis. G. L. Kelley and E. W. Evers 1052
  Monoxide, Detection of. C. R. Hoover 770
  Monoxide Detector, Tests of—in Mines. Harrington and Dyer. Gov. Pub 370
  Monoxide Poisoning in Closed Garages. Gov. Pub 1087
  Products. Tariff Information Surveys. Gov. Pub 742
  Tetrachloride, Gases Produced in Use of—and Foamite Fire Extinguishers in Mines. Fieldner and Katz. Gov. Pub 854
Carbonization:
  Low-Temperature, and Its Application to High Oxygen Coals. S. W. Parr and T. E. Layng. (*Correction*, 266) 14
  Low-Temperature, Commercial Realization of—of Coal. H. A. Curtis 23
  Of Canadian Lignite. E. Stansfield 17
  Of Lubricating Oils. Gov. Pub 272
  Some Factors Affecting Sulfur Content of Coke and Gas in—of Coal. A. R. Powell 33
Carbons, Decolorizing, Effect of Some—upon Color and Colloids of Cane Juice. J. F. Brewster and W. G. Raines, Jr 921
Carbo-Sulfhydryl Accelerators and Action of Zinc Oxide. Reactions of Accelerators during Vulcanization, III. C. W. Bedford and L. B. Sebrell 1034
Carvacrol, Comparative Toxicity of—and Thymol (Isothymol). Livingston. Gov. Pub 743
Casein, Alkaline Hydrolysis of. M. A. Griggs 1027
Casein, Grain-Curd, Precipitation of—from Pasteurized Milk, Including Sweet Cream Buttermilk. H. F. Zoller 510
Catalysis: Mechanism of Catalytic Processes. H. S. Taylor 75
Cathodes, Gold, for Electrolytic Work. A. B. Andrews 560
Cattle Food, Preparation and Analysis of—Consisting of Hydrolyzed Sawdust. E. C. Sherrard and G. W. Blanco 61
Cell, Modified, for Ultramicroscope. C. C. Kiplinger 713
Celluloid, Camphor Substitutes in Manufacture of. A. P. Sachs and O. Byron 893
Cellulose:
  Acetate, European Practice in—and Dopes during War. P. Drinker 831
  Chemistry, Section of. Report, New York Meeting, A. C. S. G. J. Esselen, Jr 959
  Corncob, Possible Uses of—in Explosives Industry. L. G. Marsh 296
  Estimation of—in Wood. B. Johnsen, S. A. Mahood and W. H. Dore. [*See* This Journal, **12** (1920), 264, 873] 358
  Mucilage. J. E. Minor 131
  Studies on Bast Fibers. II—Cellulose in Bast Fibers. Y. Uyeda 141
  Studies on Chemistry of. I—Constitution of Cellulose. H. Hibbert 256, 334

Cement. Gov. Pub.:
  In 1919. Burchard ... 1088
  Lime and —, Developing Standard Specifications for Paper Bags for. Houston ... 581
  Lime, Gypsum and. Tariff Information Survey ... 742
  Portland, Effects of Cal as Accelerator of Hardening of. Young ... 177
  Portland, Standard Specifications and Tests for ... 743
Census Bureau. Gov. Pub ... 490
Ceramic Chemistry, Selected Bibliography of Books, in English Language, Dealing with—and Ceramic Industries. E. W. Washburn, C. W. Parmelee and R. K. Hursh ... 476
Ceramics: National Research Council, Division of Chemistry and Chemical Technology, Committee on Ceramic Research. Note ... 571
Chandler, C. F. Editorial Note ... 5
Chandler, C. F., Receives National Institute of Social Sciences Medal. 530
Charcoal, Artificially Dense, Production of. L. F. Hawley ... 301
Charcoal Method of Gasoline Recovery. G. A. Burrell, G. G. Oberfell and C. L. Voress. Note ... 58
Chaulmoogra Oil, Fractionation of. Dean and Wrenshall. Gov. Pub. ... 490, 743
Cheese, Microscopic Study of Bacteria in. Hucker. Gov. Pub ... 1175
Cheese, Swiss, Relation of Hydrogen-Ion Concentration to Heat Coagulation of Proteins in—Whey. Y. Okuda and H. F. Zoller ... 515
Chemical Education, Meeting of Section of. New York Meeting, A. C. S. J. C. Olsen ... 1074
Chemical Education, Section of. Report, New York Meeting, A. C. S. N. E. Gordon ... 959
Chemical Engineering Catalog. Equitable Distribution. Editorial ... 5
Chemical Engineering Practice, School of—of Massachusetts Institute of Technology. R. T. Haslam ... 465
Chemical Foundation Patents, Dyes Derived from β-Oxynaphthoic Acid and from J-Acid, with Reference to. A. W. Joyce ... 946
Chemical Glassware. Elementary Economics. Editorial ... 107
  Square Dealing. Editorial ... 974
Chemical Industries, Seventh National Exposition of. (*See* Exposition)
Chemical Industry and Trade of England, 189; France, 6; Holland, 593; Switzerland. O. P. Hopkins ... 285
Chemical Industry in China. W. H. Adolph ... 1099
Chemical Plant Equipment Manufacturers:
  Meeting, New York City, September 17, 1921 ... 892
Chemical Salesman's Association ... 806
  1st Annual Banquet, New York City, September 15, 1921 ... 892
Chemical Warfare. Danger Ahead. Editorial ... 974
Chemical Warfare Service:
  A. C. S. Advisory Committee Resolution. Note ... 109
  Editorial Note ... 405
  Sowing Good Seed. Editorial ... 266
Chemicals and Dyes, Importations of. Gov. Pub ... 1087
Chemicals, Definition of Limits for Impurities in. Sulfate in Nitric Acid. W. D. Collins ... 948
Chemicals, Oils and Paints, Reclassification of. Gov. Pub ... 659
Chemicals, Our Foreign Trade in. O. P. Hopkins ... 753
Chemistry and Disarmament ... 1171
Chemistry, Biggest Things in. Perkin Medal Acceptance Address. W. R. Whitney ... 161
Chemistry, Immediate Needs of—in America. W. J. Hale ... 460
Chemistry in the United States. Address, Rochester Meeting, A. C. S. C. F. Chandler ... 391
Chemistry, Place of—in Business. Address, Rochester Meeting, A. C. S. A. D. Little ... 386
Chemists' Club:
  Anniversary Celebration. Announcement. C. Baskerville ... 267
  Bureau of Employment. Report ... 563
  Confers Honorary Membership ... 355
China, Chemical Industry in. W. H. Adolph ... 1099
Chloride Volatilization Process. Varley. Gov. Pub ... 660
Chlorides, Determination of—in Petroleum. R. R. Matthews ... 325
Chlorine, Apparatus for Rapid Determination of Available—in Bleach Liquor. M. Schrero ... 559
Chlorine: Death Erroneously Attributed to Chlorinated Water. Emerson. Gov. Pub ... 1174
Chlorine Disinfectants, Germicidal Value of. Tilley. Gov. Pub ... 98
Chlorine Products. Tariff Information Surveys. Gov. Pub ... 659
Chlorites, Chromium-Bearing, California, and Wyoming. Shannon. Gov. Pub ... 175
Chrome Liquor, Effect of Concentration of—upon Adsorption of Its Constituents by Hide Substance. A. W. Thomas and M. W. Kelly ... 65
Chrome Ores, Pennsylvania, Maryland, and North Carolina. Knopf and Lewis. Gov. Pub ... 964
Chromite Deposits in California Oregon, Washington, and Montana. Diller, *et al.* Gov. Pub ... 1087
Chromite in 1919, by Diller, 370; in 1920, by Sampson. Gov. Pub ... 965
Chromium and Vanadium, Determination of—in Ferrovanadium by Electrometric Titration. G. L. Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright ... 939
Chromium, Determination of—in Ferrochromium by Electrometric Titration. G. L. Kelley and J. A. Wiley ... 1053
Chromium, Rapid Iodometric Method for Determination of—in Chromite. E. Little and J. Costa ... 228
Cider Preservatives. R. D. Scott and E. G. Will ... 1141
Citric Acid, Manufacture of—from Lemons. C. P. Wilson ... 554
Citrus Leaves, Normal and Mottled, Composition of. Kelley and Cummins. Gov. Pub ... 272
Citrus Plants, Fumigation of—with Hydrocyanic Acid. Woglum. Gov. Pub ... 97
Clays and Earths. Tariff Information Surveys. Gov. Pub ... 742

Coal:
  Original Papers:
    Commercial Realization of Low-Temperature Carbonization of. H. A. Curtis ... 23
    Distribution of Forms of Sulfur in—Bed. H. F. Yancey and T. Fraser ... 35
    High Oxygen, Low-Temperature Carbonization and Its Application to. S. W. Parr and T. E. Layng. (*Correction*, 266) ... 14
    Pittsburgh—, By-Product Coke and Anthracite as Fuel for Heating Houses. H. Kreisinger ... 31
  Government Publications:
    Analysis of Sulfur Forms in. Powell ... 660
    Bituminous, Structure in. Thiessen ... 272
    Cannel, in Southern Utah. Allen ... 491
    Dust Hazards in Industrial Plants. Tracy ... 581
    Eastern Idaho. Mansfield ... 176
    Factors Affecting Losses of—in Mining. Rice ... 660
    In 1918. Part B. Distribution and Consumption. Lesher ... 369
    Iowa, Analyses of. Rice, *et al.* ... 491
    Paleozoic Bituminous, Structure in. Thiessen ... 177
    San Juan County, New Mexico. Bauer and Reeside, Jr. ... 369
    Thomas Bed near Harrison, West Virginia. Campbell ... 369

Coal Mines:
  Government Publications:
    Bituminous, Causes and Prevention of Fires and Explosions in. Steidle ... 271
    Fatalities in 1920. Adams ... 272
    Fatalities in U. S., 1920, and Statistics Supplementing *Bull.* 115. Adams ... 660
    Fatalities in U. S., Monthly Statement of. Adams. August and September (1920), 97; October and November, 271; March (1921), 743; April, 854; May, 965; June ... 1089
    Operating Regulations, Act of February 25, 1920 ... 965
    State Mining Laws on Use of Electricity in and about. Ilsley ... 271
Coal-Tar Chemical Industry. Effective Help. Editorial ... 751
Coal-Tar: Chemistry of Acenaphthene and Derivatives. D. A. Hahn and H. E. Holmes ... 822
Coal-Tar, Detection and Estimation of—Oils in Turpentine. V. E. Grotlisch and W. C. Smith ... 791
Cobalt and Nickel, Determination of—in Cobalt Steels. G. E. F. Lundell and J. I. Hoffman ... 540
Cobalt Oxides, Colors Developed by. H. J. Witteveen and E. F. Farnau ... 1061
Cocaine. Tariff Information Surveys. Gov. Pub ... 659
Coffee Bean (*Daubentonia longifolia*), a Poisonous Plant. Marsh and Clawson. Gov. Pub ... 370
Coke, By-Product—, Anthracite, and Pittsburgh Coal as Fuel for Heating Houses. H. Kreisinger ... 31
Coke in 1918. Lesher and Tryon. Gov. Pub ... 580
Coke-Oven Accidents in U. S., 1920. Adams. Gov. Pub ... 1089
Coking, By-Product. F. W. Sperr, Jr., and E. H. Bird ... 26
Cold Test Apparatus for Oils. G. H. P. Lichthardt ... 145
College of the City of New York, Lectures at ... 345
Colloid Chemistry, Research Problems in. W. D. Bancroft ... 83, 153, 260, 346
Colloid Development. H. N. Holmes ... 357
Colloidal Fuels, Preparation and Properties. S. E. Sheppard ... 37
Colloidal Material, Methods for Determining Amount of—in Soils. C. J. Moore, W. H. Fry and H. E. Middleton ... 527
Color, Measurement of. Address, Rochester Meeting, A. C. S. C. E. K. Mees ... 729
Color Work, Selection of Analysts for—in Chemistry. O'Brien. Gov. Pub ... 965
Column, Fractionating. P. Gross and A. H. Wright ... 701
Colza, Chinese. Mustard Seeds and Substitutes, I. Viehoever, *et al.*, Gov. Pub ... 98
Combustion, Rapid Dry—Method for Simultaneous Determination of Soil Organic Matter and Organic Carbon. J. W. Read ... 305
Combustion Smokes. G. A. Richter ... 343
Commerce Reports. November (1920), 98; December, 177; January (1921), 272; February, 370; March, 492; April, 581; May, 661; June, 743; July, 854; August, 965; September, 1090; October ... 1175
Concrete, Pouring and Pressure Tests of. Slater and Goldbeck. Gov. Pub ... 177
Concrete Stone and Concrete Blocks in 1919. Loughlin and McCaslin. Gov. Pub ... 964
Condensation Temperatures of Gasoline- and Kerosene-Air Mixtures. R. E. Wilson and D. P. Barnard, 4th ... 906
Condenser, Combined Reflux, Extractor, Still and Autoclave. A. T. Shohl and M. L. Koch ... 819
Conductivity, Electrical, of Solutions of Zinc Sulfate in Presence of Sulfuric Acid. H. V. Tartar and H. E. Keyes ... 1127
Conductivity, Electrical, of Water Extracts. Studies of Wheat Flour Grades, I. C. H. Bailey and F. A. Collatz ... 319
Congressional Committees. Gov. Pub ... 271, 369, 490, 1087
Conifers, Pacific Coast, Tannin Content of. R. H. Clark and H. I. Andrews ... 1026
Constant Temperature Rooms. E. G. Hastings ... 1056
Containers. Gov. Pub ... 369

Copper:
  Absorption of—from Soil by Potato Plants. Cook. Gov. Pub ... 1175
  Advance Statement of Production in U. S., 1920. Jenison. Gov. Pub ... 964
  Compressed Air Operated Ventilation Doors in—Mines. Gardner. Gov. Pub ... 1089
  Copper and Brass Research Association. Note ... 918
  Estimation of Small Quantities of Gold, Silver and Platinum Metals in Material High in. Davis. Gov. Pub ... 491
  In 1919. General Report. Jenison. Gov. Pub ... 1088
  Production (1919). Gov. Pub. Eastern States, by Dunlop, 175; Alaska, by Brooks and Martin; California and Oregon, by Yale, 580; Central States, by Dunlop, 659; Arizona and Utah, by Heikes, 965; Idaho, by Gerry; Nevada, by Heikes; Montana, by Gerry, 1087; South Dakota and Wyoming, by Henderson ... 1174
    (1920) Eastern States, by Dunlop ... 1087
  Thermal Expansion of—and Alloys. Hidnert. Gov. Pub ... 743
Corks, Protection of. P. Gross and A. H. Wright ... 702
Corn:
  Government Publications:
    Assimilation of Nitrogen, Phosphorus, and Potassium by. Gile and Carrero ... 965
    Losses during Ensiling of. Shaw, *et al* ... 661
    Reliability of the Nail Test for Predicting the Chemical Composition of Green Sweetcorn. Appleman ... 1174

Corncob Cellulose, Possible Uses of—in Explosives Industry. L. G. Marsh ... 196
Corncob Extract, Aqueous, Production of Furfural by Action of Superheated Water on. F. B. LaForge ... 1024
Corncobs, Fermentation Process for Production of Acetic and Lactic Acids from. E. B. Fred and W. H. Peterson ... 211
Corncobs, Fermentation Process for Production of Acetone, Alcohol, and Volatile Acids from. W. H. Peterson, E. B. Fred and J. H. Verhulst ... 757
Cornell Chemical Laboratory. Note ... 1169
Corrosion, Methods for Preventing—of Metal Parts of Airplanes. Gov. Pub ... 964
Corundophilite and Amesite, Chester, Mass. Shannon. Gov. Pub ... 175
Cost Factors, Special, and Their Relation to Development of Our Organic Chemical Industry. G. DuBois ... 1159
Cotton: Crop Protection Institute Discusses War on Boll-Weevil ... 89

- Cotton Fabric, Effect of Certain Fire-Proofing Solutions on. R. L. Sibley 676
- Cottonseed, Composition of. Creswell and Bidwell. Gov. Pub. 1174
- Cottonseed Oil Industry, American, Survey of. Gov. Pub. 271
- Coumarins, Production of—from Maleic and Malic Acids. G. C. Bailey and F. Boettner 905
- Creosote, Coal-Tar, Toxicity of Various Fractions and Combinations of Fractions of—to Wood-Destroying Fungi. H. Schmitz and S. M. Zeller 621
- Crop Protection Institute:
  - Meeting, New York City, December 6, 1920, Discussion of War on Boll-Weevil 89
- Crucibles: Uniform High Temperature throughout a Large Volume. E. F. Northrup 639
- Cryogenic Laboratory, Bureau of Mines. Note 560
- Cryolite and Fluorspar in 1919, 964; in 1920. Davis. Gov. Pub. 964
- Cryoscopy of Milk. J Hortvet 198
- Curie, Madame:
  - Honored by Chemical Societies 568
  - Receives Gram of Radium and Many Honors 573
  - Reception 468
  - Welcome. Editorial 502
- Cyanide Gas Generator, Portable. Fauntleroy. Gov. Pub. 1174

- DATURA stramonium, Atropine Sulfate from. H. W. Rhodehamel and E. H. Stuart 218
- Dayton Process. F. C. Binnall 242
- Decolorization, Effect of Varying Hydrogen-Ion Concentration upon—of Cane Juice with Carbon. J. F. Brewster and W. G. Raines, Jr. 1043
- Dehydration: Effect of Heat on Different Dehydrated Vegetables. C. E. Mangels and H. C. Gore 525
- Denigès Test, Improved, for Detection and Determination of Methanol in Presence of Ethyl Alcohol. R. M. Chapin 543
- Department of Agriculture. Gov. Pub. 97, 177, 272, 370, 492, 581, 660, 743, 854, 1174
- Department of Labor. Gov. Pub. 97
- Desugarization, Comparison of Results in—with Steffen Lime, Barium and Strontium Processes. M. Potvliet 1041
- Detonators, Low-Grade Foreign, Dangers in Using. Munroe. Gov. Pub. 491
- Dextrin, Consistency of Starch and—Pastes. W. H. Herschel and C. Bergquist 703
- Dicyanodiamide, Determination of—and of Urea in Fertilizers. E. Johnson 533
- Digester, Rotary, for Use in Bagasse Analysis. G. L. Spencer 640
- Diphenylamine, Melting Point of. H. Rogers, W. C. Holmes and W. L. Lindsay 314
- Disinfectant Testing by Hygienic Laboratory Method. Gov. Pub. 964
- Disinfectants, Chlorine, Germicidal Value of. Tilley. Gov. Pub. 98
- Distillation Apparatus. P. Gross and A. H. Wright 701
- Dopes, European Practice in Cellulose Acetate and—during War. P. Drinker 831
- Drugs:
  - Atropine Sulfate from *Datura stramonium.* H. W. Rhodehamel and E. H. Stuart 218
  - Benzyl Succinate. M. Bye 217
  - Drug Plants under Cultivation. Stockberger. Gov. Pub. 1174
  - Studies in Synthetic Drug Analysis. VIII—Estimation of Salicylates and Phenol. W. O. Emery 538
  - Tariff Information Surveys. Gov. Pub. 659, 742
- Dry Substance in Molasses, Sirups and Juices by Spencer Electric Oven. G. P. Meade 924
- Dryers and Drying (*See* A. C. S. Rochester Meeting, Symposium)
- Dumas, Modification of—Method, and Application of Kjeldahl Method to Determination of Nitrogen in Nitronaphthalenes. P. H. M.-P. Brinton, F. M. Schertz, W. G. Crockett and P. P. Merkel 636
- Dustiness, Air, Experiments in Control of. Spencer. Gov. Pub. 175
- DYESTUFFS:
  - *Addresses and Original Papers:*
    - Anilides of β-Oxynaphthoic Acid. E. R. Brunskill 309
    - Application of Maleic and Fumaric Acids and Their Salts in Textile Industry. J H Carpenter 410
    - Benzenedisulfonic Acid from Benzenemonosulfonic Acid. C. E. Senseman 1124
    - Contribution to Estimation of H-Acid. H. R. Lee 1049
    - Dyes Derived from β-Oxynaphthoic Acid and from J-Acid, with Reference to Chemical Foundation Patents. A. W. Joyce. 946
  - *Editorials:*
    - Call to Service 503
    - Congressional Recognition of Chemistry 592
    - Facts Supplant General Statements 590
    - Fight in the Senate 750
    - Road to Demoralization 108
    - Specific Facts 283
    - The Race Is not Always to the Swift 109
    - Thinking It Through 186
    - Tragedy Averted 502
    - Will the Senate Act? 2
  - *Government Publications:*
    - Census of—and Coal-Tar Chemicals 1920 664
    - Dyes and Dyeing 369
    - Importations of—and Chemicals 1087
    - Natural Dyes. Tariff Information Surveys. Gov. Pub. 659
  - *Notes:*
    - British Dye Bill 169
    - British Dyestuffs Committee 313
    - Dye Chemistry, Division. Report, New York Meeting, A. C. S. R. N. Shreve 958
- Dynamite, Ditching with. Gov. Pub. 490

- EDITORIALS 2, 107, 186, 282, 502, 590, 670, 750, 974, 1098
  (*See* HERTY, C. H., in AUTHOR INDEX for Complete List of Titles; Subjects treated will be found in this Index)
- Eggs. Gov. Pub. 369
- Electric Muffle Furnaces for Laboratory Use. H. C. Kremer 561
- Electrolytic Cell, New Type of. H. S. Lukens 562
- Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese. R. E. Wilson, W. G. Horsch and M. A. Youtz. (*Correction,* 960) 763
- Electrometric Titration, Determination of Chromium in Ferrochromium by. G. L. Kelley and J. A. Wiley 1053
- Electrometric Titration, Determination of Vanadium and Chromium in Ferrovanadium by. G. L. Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright 939
- Employment of Women in Hazardous Industries in U. S. Gov. Pub. 97
- Emulsions. (*See* also A. C. S., New York Meeting, Symposium)
- Emulsions: Dehydration of Tar in the Laboratory. W. J. Huff 1123
- ENGLAND, CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins 189
- Enzymes, Properties and Action of—in Relation to Leather Manufacture. J. T. Wood 1135
- Ethyl Alcohol, Improved Denigès Test for Detection and Determination of Methanol in Presence of. R. M. Chapin 543
- Ethyl Chloride, Rate of Evaporation of—from Oils. C. Baskerville and M. Hirsh 322
- Ethylene, Preparation of—by Hydrogenation of Acetylene. W. H. Ross, J. B. Culbertson and J. P. Parsons 775
- European Relief Council. Note. W. H. Nichols 169
- Explosion and Fire Hazard in Dusty Industries. Unprotected Electric Lights. Price and Brown. Gov. Pub. 661
- Explosion in High-Pressure Compressed-Air Line. Gardner. Gov. Pub. 491
- Explosions, Laboratory, Liability for 1079
- EXPLOSIVES:
  - Fees for Testing—and Conditions and Requirements under Which Explosives Are Tested. Gov. Pub. 177
  - Fulminates and. Tariff Information Surveys. Gov. Pub. 964
  - National Research Council, Division of Chemistry and Chemical Technology, Committee on Explosives Investigations. Note 571
  - Picric Acid as Blasting Agent. Munroe and Howell. Gov. Pub. 581
  - Possible Uses of Corncob Cellulose in—Industry. L. G. Marsh 296
  - Regulation of—in U. S. Munroe. Gov. Pub. 491
- EXPOSITION OF CHEMICAL INDUSTRIES, SEVENTH NATIONAL:
  - New York, September 12 to 17, 1921. Announcement, 572; General Program, 654; Papers, 735; Editorial, 752; Program, 846; Report, 886; Formal Addresses, 888; Features of Exposition Week 891
  - Relation of Our Chemical Industry to Our National Defense. Address. I. L. Lenroot 888
- Extractor, Combined—, Reflux Condenser, Still and Autoclave. A. T. Shohl and M. L. Koch 819

- FATS and Oils, Animal and Vegetable, Production, Consumption, Imports, Exports, 1919 and 1920. Gov. Pub. 490
- Fats and Oils, Animal and Vegetable. Tariff Information Surveys. Gov. Pub. 659
- Fats and Oils, Test for Annatto in. W. Brinsmaid 216
- Federal Trade Commission. Gov. Pub. 490, 659
- Feldspar in 1919. Beach. Gov. Pub. 1087
- Fellowships:
  - American Field Service, for French Universities 1126
  - Industrial, at Mellon Institute 478
  - Research, American Institute of Baking. Note 92
  - Viscosity and Temperature of Fused Glass, University of Illinois. Note 571
- Fermentation Process for Production of Acetic and Lactic Acids from Corncobs. E. B. Fred and W. H. Peterson 211
- Fermentation Process for Production of Acetone, Alcohol, and Volatile Acids from Corncobs. W. H. Peterson, E. B. Fred and J. H. Verhulst 757
- Ferroalloy Industries. Tariff Information Surveys. Gov. Pub. 742
- Ferrochromium, Determination of Chromium in—by Electrometric Titration. G. L. Kelley and J. A. Wiley 1053
- Ferromanganese, Electrolytic Production of Sodium and Potassium Permanganates from. R. E. Wilson, W. G. Horsch and M. A. Youtz. (*Correction,* 960) 763
- Ferrovanadium, Determination of Vanadium and Chromium in—by Electrometric Titration. G. L. Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright 939
- Fertilizer Chemistry, Division. Report, New York Meeting, A. C. S. H. C. Moore 957
- FERTILIZERS:
  - Atmospheric Nitrogen for. Davis. Gov. Pub. 272
  - Boron in Relation to Fertilizer Industry. J. E. Breckenridge 324
  - Determination of Dicyanodiamide and of Urea in. E. Johnson 533
  - Fertilizer Situation. Gov. Pub. 490
  - Phosphorus in. Waggaman. Gov. Pub. 1174
  - Potash Shales of Illinois. M. M. Austin with S. W. Parr 1144
  - Raw Materials. Tariff Information Surveys. Gov. Pub. 742
  - Relation of Sulfates to Plant Growth and Composition. Miller. Gov. Pub. 1175
  - Studies of Availability of Organic Nitrogenous Compounds, I. Charles S. Robinson, O. B. Winter and E. J. Miller 933
- Filter Paper, American Made. Editorial Note 405
- Filter Paper, Note on Effect of Presence of—on Permanganate-Oxalate Titrations. S. G. Simpson 1152
- Filtration (*See* also A. C. S., New York Meeting, Symposium)
- Filtration, Study of Fundamental Laws of—Using Plant-Scale Equipment. F. P. Baker. (*See* Sperry, 1163) 610
- Fire Blanket Receptacle. L. S. Bushnell 1081
- Fire Engine Hose, Ignition of—When in Use. Note. A. H. Gill 168
- Fire Extinguishers, Gases Produced in Use of Carbon Tetrachloride and Foamite—in Mines. Fieldner and Katz. Gov. Pub. 854
- Fire-Proofing, Effect of Certain—Solutions on Cotton Fabric. R. L. Sibley 676
- Fish, Preservation of—Frozen in Chilled Brine. I—Penetration of Salt. L. H. Almy and E. Field 927
- Flask, Microdistilling. P. Gross and A. H. Wright 702
- Flotation, Consumption of Reagents Used in. Varley. Gov. Pub. 370
- Flour, Wheat, Studies of—Grades:
  - I—Electrical Conductivity of Water Extracts. C. H. Bailey and F. A. Collatz 319
  - II—Buffer Action of Water Extracts. C. H. Bailey and A. C. Peterson 916
- Fluorspar and Cryolite in 1919, 964; in 1920. Davis. Gov. Pub. 964
- Fluorspar Industry in 1919-20. Davis and Ladoo. Gov. Pub. 491
- Fluorspar, Separation of Sphalerite, Silica, and Calcite from. Gross. Gov. Pub. 965
- Food Research Institute 302, 479
- FOODS: (*See* also Milk, Sugars)
  - Annatto, Test for—in Fats and Oils. W. Brinsmaid 216
  - Cheese, Microscopic Study of Bacteria in. Hucker. Gov. Pub. 1175
  - Cheese, Swiss, Relation of Hydrogen-Ion Concentration to Heat Coagulation of Proteins in—Whey. Y. Okuda and H. F. Zoller 515

  - Fish, Preservation of—Frozen in Chilled Brine. I—Penetration of Salt. L. H. Almy and E. Field 927
  - Grape Pomace and Stems, Commercial Utilization of—from Grape-Juice Industry. Rabak and Shrader. Gov. Pub 743
  - Grapefruit, Florida, Changes in—in Storage. Hawkins and Magness. Gov. Pub 177
  - Legumes, Commonly Grown, Manganese in. J. S. Jones and D. E. Bullis 524
  - Meats, Substitute for Sucrose in Curing. Hoagland. Gov. Pub 272
  - Mustard Seeds and Substitutes: I—Chinese Colza. Viehoever, *et al*. Gov. Pub 98
  - Olives, Canned Ripe, Bacteriological Study of. Koser. Gov. Pub 177
  - Pickles, Fermented. Le Fevre. Gov. Pub 272
  - Potato Plants, Absorption of Copper from Soil by. Cook. Gov. Pub 1175
  - Potatoes, Composition of Tubers, Skins and Sprouts. Cook. Gov. Pub 370
  - Potatoes, Freezing Injury to—When Undercooled. Wright and Taylor. Gov. Pub 743
  - Potatoes, Mineral Constituents of—and Potato Flour: Effect of Process of Manufacture on Composition of Ash of Potato Flour. C. E. Mangels 418
  - Potatoes, Sweet, Canned, Discoloration in. E. F. Kohman 634
  - Potatoes, Sweet, Reduction in Strength of Mercuric Chloride Solution Used for Disinfecting. Weimer. Gov. Pub 965
  - Sardine Industry, Maine. Weber, *et al*. Gov. Pub 272
  - Shortening: Its Definition and Measurement. C. E. Davis 797
  - Vanilla Extracts, New Lead Number Determination in. H. J. Wichmann 414
  - Vegetables, Dehydrated, Effect of Heat on Different. C. E. Mangels and H. C. Gore 525
  - Vegetables, Raw-Dried, Relation of Moisture Content to Deterioration of—upon Common Storage. H. C. Gore and C. E. Mangels 523
  - Vitamines, Chemistry of. A. Seidell 72
- FOREIGN TRADE, OUR, IN CHEMICALS. O. P. Hopkins 753
- Formaldehyde. Tariff Information Surveys. Gov. Pub 659
- Formulary, National (4th ed.), Comments on U. S. Pharmacopeia IX, and—, 1917. DuMez. Gov. Pub 175
- France and Belgium, Industrial Machinery in. (With Bibliography) Wood. Gov. Pub 177
- FRANCE, CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins 6
- FUELS: (*See* also A. C. S., New York Meeting, Symposium)
  - *Addresses and Original Papers:*
    - Forests of U. S. as Source of Liquid Fuel Supply. R. C. Hawley 1059
    - Motor Fuel from Vegetation. T. A. Boyd 836
    - Role of Chemist in Relation to Future Supply of Liquid Fuels. H. Hibbert 841
    - Total Sensible Heats of Motor Fuels and Their Mixtures with Air. R. E. Wilson and D. P. Barnard, 4th 912
  - *Government Publications:*
    - Aviation Gasoline, Specifications and Methods of Testing 97
    - Briquets in 1920. McKenney 1088
    - Care and Operation of Fuel Oil-Burning Installations 97
    - Comparison of Alcogas Aviation Fuel with Export Aviation Gasoline. Gage, *et al* 97
    - Comparison of Hector Fuel with Export Aviation Gasoline. H. C. Dickinson, *et al* 97
    - Contributions to Economic Geology, 1919. Part II, Mineral Fuels. White and Ashley 271
- Fuller's Earth in 1919, 491; in 1920. Middleton. Gov. Pub 1088
- Fulminate, Mercury, as Skin Irritant, III. Livingston. Gov. Pub 175
- Fumaric and Maleic Acids, Applications of—and Their Salts in Textile Industry. J. H. Carpenter 410
- Fumigation of Citrus Plants with Hydrocyanic Acid. Woglum. Gov. Pub 97
- Fumigation: Portable Cyanide Gas Generator for Fumigating Small Compartments. Fauntleroy. Gov. Pub 1174
- Furfural, Preparation and Technical Uses of. K. P. Monroe 133
- Furfural, Production of—by Action of Superheated Water on Aqueous Corncob Extract. F. B. LaForge 1024
- Furnaces, Electric Muffle, for Laboratory Use. H. C. Kremers 561

- GAGE, Vacuum. P. Gross and A. H. Wright 702
- Galactose, Preparation of. Clark. Gov. Pub 1089
- GAS:
  - *Editorials and Original Papers:*
    - Analysis, Formation of Oxides of Nitrogen in Slow Combustion and Explosion Methods in. G. W. Jones and W. L. Parker 1154
    - Artificial, Enrichment of—with Natural Gas. J. B. Garner 58
    - Dayton Process. F. C. Binnall 242
    - Gas Light Papers. A Special Problem. Editorial 188
    - Lachrymal. Experimental Evidence. Editorial 752
  - *Government Publications:*
    - Better Gas with Less Natural Gas in Domestic Gas Appliances 1089
    - Helium-Bearing Natural. Rogers 580
    - Masks for Gases Met in Fighting Fires. Fieldner, *et al* 660
    - Natural, and Blue Water, Stenches for Detecting Leakage of. Katz and Allison 177
    - Natural, Chlorination of. Jones, *et al*. 271
    - Natural—Resources of Central North Texas. Shaw and Ports 176
    - Oil and—Field, Lance Creek, Wyoming. Hancock 176
    - Oil and—Permits, Regulations Concerning 175
    - Oil and—Resources and Structure of Osage Reservation. Goldman and Robinson 176
    - Service, Standards for. 492
    - Well, Method of Controlling—, Alkali Butte, Wyoming. Tough 491
- GASES:
  - Carbon Dioxide, Free and Combined, Method for Determination of. J. A. Shaw 1151
  - Carbon Dioxide, Solid Sodium Hydroxide as Absorbent for—in Steel Analysis. G. L. Kelley and E. W. Evers 1052
  - Carbon Monoxide, Detection of. C. R. Hoover 770
  - Carbon Monoxide Poisoning in Closed Garages. Gov. Pub 1087
  - Fuels and—, Symposium on Chemistry of. Division of Industrial and Engineering Chemistry. Report, New York Meeting, A. C. S. R. S. McBride 956
  - Permeation of Oxygen Breathing Apparatus by—and Vapors, Fieldner, *et al*. Gov. Pub 660
  - Pressure-Volume Deviation of Methane, Ethane, Propane and Carbon Dioxide at Elevated Pressures. Burrell and Jones. Gov. Pub 1089
  - Rock Strata—in Mines of East Tintic Mining District, Utah. McElroy. Gov. Pub 1089
- GASOLINE:
  - *Original Papers:*
    - Calcium Chloride Method for Determination of Water in—and in Certain Other Substances. C. W. Clifford 628
    - Charcoal Method of—Recovery. G. A. Burrell, G. G. Oberfell and C. L. Voress. Note 58
    - From Natural Gas. V—Hydrometer for Small Amounts of Gasoline. R. P. Anderson and C. E. Hinckley 144
    - Iodine Numbers of Cracked—and Unsaturated Hydrocarbons. W. F. Faragher, F. H. Garner and W. A. Gruse 1044
    - Kerosene and—Air Mixtures, Condensation Temperatures of. R. E. Wilson and D. P. Barnard, 4th 906
    - Losses Due to Incomplete Combustion in Motor Vehicles. A. C. Fieldner, A. A. Straub and G. W. Jones 51
    - Solubility of Water in—and in Certain Other Organic Liquids, Determined by Calcium Chloride Method. C. W. Clifford 631
  - *Government Publications:*
    - Explosion, Memphis, Tenn., January 24, 1921. Dow 491
    - Motor, 3rd Semiannual—Survey, 491; 4th. Smith 1089
    - Natural-Gas, Treating—to Meet "Doctor Test." Dow 271
    - Quality of—Marketed in the U. S. Hill and Dean 271
- Gelatins, Commercial, Gold Number of. F. A. Elliott and S. E. Sheppard 699
- Gelatins, Setting and Melting Points of. S. E. Sheppard and S. Sweet 423
- Gems and Precious Stones in 1919. Stoddard. Gov. Pub 490
- General Land Office. Gov. Pub 175
- Generator, Portable Cyanide Gas, for Fumigating Small Compartments. Fauntleroy. Gov. Pub 1174
- Geological Survey:
  - Director's Annual Report, June 30, 1920. Gov. Pub 176
  - Government Publications. 175, 271, 369. 490, 580, 659, 743, 964, 1087, 1174
- Geology: Economic, Contributions to—, 1919:
  - I—Metals and Nonmetals except Fuels. Ransome and Burchard. Gov. Pub 176
  - II—Mineral Fuels. White and Ashley. Gov. Pub 271
- Germany and Japan. Amenities de Luxe. Editorial 3
- Glass, Lead, Graded Seal for Joining Pyrex to. W. C. Taylor and A. Bailey 1158
- Glazes, High Fire Porcelain. Sortwell. Gov. Pub 1089
- Glucose, New Qualitative Test for Sucrose in Presence of. L. A. Congdon and C. R. Stewart 1143
- Glycerol, Need of New Table for Specific Gravity and Per cent of. L. W. Bosart 944
- GOLD:
  - *Original Paper:*
    - Gold Number of Commercial Gelatins. F. A. Elliott and S. R. Sheppard 699
  - *Government Publications:*
    - Congressional Committee Hearings 490
    - Estimation of—in Material High in Copper. Davis 491
    - Production (1919). Eastern States, by Dunlop, 175; Alaska, by Brooks and Martin; California and Oregon, by Yale, 580; Arizona and Utah, by Heikes, 965; Idaho, by Gerry; Nevada, by Heikes; Montana, by Gerry, 1087; South Dakota and Wyoming, by Henderson 1174
      - (1920) Eastern States, by Dunlop 1087
    - Recovery, Comparison of Methods of—from Black Sand. Gross. 272
- Government Printing Office. Gov. Pub 175
- GOVERNMENT PUBLICATIONS. N. A. Parkinson 97, 175, 271, 369, 490, 580, 659, 742, 854, 964, 1087, 1174
- Granite-Working Plants, Dust in Air of. Katz. Gov. Pub 491
- Grape Pomace, Utilization of—from Grape-Juice Industry. Rabak and Shrader. Gov. Pub 743
- Grape-Seed Oil. F. Rabak 919
- Grapefruit, Florida, Changes in—in Storage. Hawkins and Magness. Gov. Pub 177
- Graphite:
  - Determination of Volatile Matter in. O. L. Shinn 633
  - Foreign, in 1919. Redfield. Gov. Pub 490
  - In 1919. Beach. (History of Graphite Mining in Pennsylvania, F. Bascom) Gov. Pub 964
  - In 1920. Beach. Gov. Pub 1088
- Grass, Sudan, Hydrocyanic Acid in. Swanson. Gov. Pub 1175
- Grasselli Medal Award 1158
- Gravel and Sand in 1919. Stone Gov. Pub 271
- Greensand, Action of Lime on. R. N. Shreve 693
- Gypsum in 1919, 176; in 1920. Stone. Gov. Pub 1088
- Gypsum: Properties, Definitions and Uses. Gov. Pub 492

- H-ACID, Contribution to Estimation of. H. R. Lee 1049
- Hardness, Modulus of—of Vulcanized Rubber. H. P. Gurney 707
- Harrison Antinarcotic Act, Section 2. Gov. Pub 175
- Harrison, Sir John, Honors to. Note 632
- Health and Safety, Miners', Almanac 1921. Williams. Gov. Pub 177
- Health Hazard, Tellurium as—in Industry. Shie and Deeds. Gov. Pub 175
- Heats, Total Sensible, of Motor Fuels and Their Mixtures with Air. R. E. Wilson and D. P. Barnard, 4th 912
- Helium-Bearing Natural Gas. Rogers. Gov. Pub 580
- Helium, Discovery of—and What Came of It. Abbott. Gov. Pub 271
- Hemp: Studies on Bast Fibers. II—Cellulose in Bast Fibers. Y. Uyeda 141
- Hexabromide and Iodine Numbers, Quantitative Determination of Linseed Oil in Mixtures with Soy-Bean by Means of—of Fatty Acids. E. A. Tschudy 941
- Hexabromide Test: Study on Oil Bromide Test of Linseed Oil. T. A. Davidson 801, 849
- Hexamethylenetetramine Compounds, Phenolic, Further Studies on. M. Harvey and L. H. Baekeland 135
- Hide Substance, Effect of Concentration of Chrome Liquor upon Adsorption of Its Constituents by. A. W. Thomas and M. W. Kelly 65
- Hides and Leather in France. Hertz. Gov. Pub 97
- Highway Materials, Sampling and Testing. Gov. Pub 1174
- Hoffmann and Bloede Scholarships of Chemists' Club. Note 480
- HOLLAND, CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins 593
- Hollyhock Seed, Composition of—and Oil. R. S. Hiltner and L. Feldstein 635
- Humidity Control by Means of Sulfuric Acid Solutions, with Critical Compilation of Vapor Pressure Data. R. E. Wilson 326
- Hydrochloric, Proposed Specification for Sulfuric, Nitric, and—Acids, and for Ammonium Hydroxide. Reagent Chemicals, I. W. D. Collins 735

Hydrocyanic Acid, Fumigation of Citrus Plants with. Woglum. Gov. Pub. 97
Hydrocyanic Acid in Sudan Grass. Swanson. Gov. Pub. 1175
Hydrogenation: Preparation of Ethylene by Hydrogenation of Acetylene. W. H. Ross, J. B. Culbertson and J. P. Parsons 775
Hydrometer for Small Amounts of Gasoline. Gasoline from Natural Gas, V. R. P. Anderson and C. E. Hinckley 144
Hypochlorite Process of Oyster Purification. Carmelia. Gov. Pub. 580

ICE CREAM, Sandy Crystals in. Their Separation and Identification. Zoller and Williams. Gov. Pub. 1174
Ice, Raw Water, Water Softening for Manufacture of. A. S. Behrman. 235
Iceland Spar. Bowles. Gov. Pub. 581
Illinois State Water Survey Division, Sewage Testing Station of. E. Bartow 945
Impurities, Definition of Limits for—in Chemicals: Sulfate in Nitric Acid. W. D. Collins 948
Incendiaries in Modern Warfare. A. B. Ray 641, 714
Incubating Temperatures. Bowen. Gov. Pub. 661
Indian Affairs Office. Gov. Pub. 369
Indices, Refractive, Determination of—of Oils. H. S. Simms 546
Indigo, Fusion of Phenylglycine-*o*-Carboxylic Acid for Production of. Alkali Fusions, III. M. Phillips 759
Industrial Alcohol. (*See* alcohol)
INDUSTRIAL AND AGRICULTURAL CHEMISTRY IN BRITISH WEST INDIES WITH SOME ACCOUNT OF WORK OF SIR FRANCIS WATTS. C. A. Browne 78
Industrial and Engineering Chemistry, Division of. Report, New York Meeting, A. C. S. H. E. Howe 956
INDUSTRIAL NOTES 172, 367, 487, 577, 658, 742, 853, 963, 1086, 1173
Industry, Chemical, Relation of—to Our National Defense. I. L. Lenroot. Address, 7th Exposition of Chemical Industries 888
Insecticides:
  Arsenate, Lead, Dry Method of Preparing. O. W. Brown, C. R. Voris and C. O. Henke 531
  Arsenate, Tricalcium, Preparation and Instability of. J. H. Reedy and I. L. Haag 1038
  Nicotine Sulfate as Ovicide and Larvicide. McIndoo, *et al.* Gov. Pub. 660
  Nicotine Sulfate in Dust Carrier against Truck-Crop Insects. Campbell. Gov. Pub. 370
Institute for Research in Tropical America. Note 351
Instruments, Scientific, Duty-Free. Aftermath. Editorial. [*See* THIS JOURNAL, **12** (1920), 1146] 187
Interior Department. Gov. Pub. 369
INTERNATIONAL CHEMICAL CONFERENCE, SECOND. C. Lormand 737
Iodine and Hexabromide Numbers, Quantitative Determination of Linseed Oil in Mixtures with Soy-Bean Oil by Means of—of Fatty Acids. E. A. Tschudy 941
Iodine Numbers of Unsaturated Hydrocarbons and Cracked Gasolines. W. F. Faragher, F. H. Garner and W. A. Gruse 1044
Iron and Associated Industries of Lorraine, Sarre District, Luxemburg, and Belgium. Brooks and La Croix. Gov. Pub. 271
Iron and Manganese Ores, Analyzed, Methods of Analysis. Gov. Pub. 743
Iron-Ore Resources of Europe. Roesler. Gov. Pub. 743
Iron Ores, Leaching—for Phosphorus. Winslow. Gov. Pub. 965
Ivory-Nut Shavings, Preparation of Mannose from. P. M. Horton 1040

J-ACID, Dyes Derived from β-Oxynaphthoic Acid and from—, with Reference to Chemical Foundation Patents. A. W. Joyce 946
Japan and Germany. Amenities de Luxe. Editorial 3

KELP, Potash from. [*See* THIS JOURNAL, **11** (1919), 864; **12** (1920), 682, 786] IV—Continuous Countercurrent Lixiviation of Charred Kelp. J. W. Turrentine and P. S. Shoaff 605
Kelp-Potash Plant, Summerland. Note 413
Kiln, Forest Service Water Spray Dry, Design and Installation of. Teesdale. Gov. Pub. 97
Kjeldahl Method, Note on Use of Potassium Permanganate in Determination of Nitrogen by. C. T. Dowell, W. G. Friedmann and D. C. Cochrane. [*See* THIS JOURNAL, **12** (1920), 1195] 358
Kjeldahl Nitrogen Determination, Use of Perchloric Acid as Aid to Digestion in. B. Mears and R. E. Hussey 1054
Knox, Senator. A Nation's Loss. Editorial 974

LABORATORIES, New Chemical. Note 574
LABORATORY AND PLANT 144, 231, 326, 554, 636, 701, 819, 944, 1056, 1157
Laboratory, Cornell Chemical. Note 1169
Lactic and Acetic Acids, Fermentation Process for Production of—from Corncobs. E. B. Fred and W. H. Peterson 211
Ladd, Senator E. F. Editorial Note 405
Lamps, Miners' Flame Safety, Relative Safety of Brass, Copper, and Steel Gauzes in. Ilsley and Hooker. Gov. Pub. 660
Lamps, Permissible Miners' Flame Safety, Procedure for Establishing List of. Gov. Pub. 491
Leaches, Saline, Removal of Free Acid from Nitrocellulose with Special Reference to Use of. S. E. Sheppard 1017
Leaching Vats, Iron, Repairing. Note. C. Flury 168
LEAD:
  Acetate, Precipitation of Solid Fatty Acids with—in Alcoholic Solution. E. Twitchell 806
  Arsenate, Dry Method of Preparing. O. W. Brown, C. R. Voris and C. O. Henke 531
  Determination of Small Amounts of—in Brass. F. W. Glaze 553
  In 1918. General Report, by Siebenthal, 271; 1919, by Siebenthal and Stoll. Gov. Pub. 1174
  Lead-Preserved Cane Juice, Determination of Reducing Sugars in. J. B. Harris 925
  New—Number Determination in Vanilla Extracts. H. J. Wichmann 414
  Poisoning, Relation of—in Utah to Mining. Murray. Gov. Pub. 1089
  Production (1919). Gov. Pub. Eastern States, by Dunlop, 175; Alaska, by Brooks and Martin; California and Oregon, by Yale, 580; Central States, by Dunlop, 659; Arizona and Utah, by Heikes, 965; Idaho, by Gerry; Nevada, by Heikes; Montana, by Gerry, 1087; South Dakota and Wyoming, by Henderson 1174
  (1920) Eastern States, by Dunlop 1087
  Radioactive, Problem of. Richards. Gov. Pub. 271
LEATHER:
  Leather Chemistry Division. Report, New York Meeting, A. C. S. J. A. Wilson 958
  Original Papers:
    Artificial, Nitrocellulose and Its Solutions as Applied to Manufacture of. W. K. Tucker. (*Correction*, 1082) 623
    Color Value of Tan Liquor as Function of Hydrogen-Ion Concentration. J. A. Wilson and E. J. Kern 1025
    Critical Study of Bating. J. A. Wilson and G. Daub 1137
    Determination of Tannin. J. A. Wilson and E. J. Kern 772
    Effect of Concentration of Chrome Liquor upon Adsorption of Its Constituents by Hide Substance. A. W. Thomas and M. W. Kelly 65
    Properties and Action of Enzymes in Relation to—Manufacture. J. T. Wood 1135
    Tannin Content of Pacific Coast Conifers. R. H. Clark and H. I. Andrews 1026
  Government Publications:
    Care of. Veitch, *et al.* 177, 743
    Leather and Hides in France. Hertz 97
Legumes, Commonly Grown, Manganese in. J. S. Jones and D. E. Bullis 524
Lemons, California, Composition of. Chace, *et al.* Gov. Pub. 1174
Lemons, Manufacture of Citric Acid from. C. P. Wilson 554
Lewis, G. N., Nichols Medal Awarded to 567
Liability for Laboratory Explosions 1079
Lights, Unprotected Electric. Fire and Explosion Hazard. Price and Brown. Gov. Pub. 661
"Lignin," Experimental Study of Significance of—Color Reactions. E. C. Crocker 625
Lignite, Canadian, Carbonization of. E. Stansfield 17
Lignite, New Salem—Field, Morton Co., N. D. Hancock. Gov. Pub. 659
Lime
  Action of—on Greensand. R. N. Shreve 693
  Cement and—, Specifications for Paper Bags for. Houston. Gov. Pub. 581
  Definitions and Specifications. Gov. Pub. 370
  Gypsum Cements and. Tariff Information Surveys. Gov. Pub. 742
  In 1919, Loughlin and Coon. Gov. Pub. 1089
Limekiln, Some New Features in—Construction. R. K. Meade 722
Linseed and Soy-Bean Oils, Effect of Variation in Analytical Constants of—upon Quantitative Determination of Linseed Oil in Mixtures by Means of Iodine and Hexabromide Numbers of Fatty Acids. E. A. Tschudy 941
Linseed Oil, Study on Oil Bromide Test of. T. A. Davidson 801, 849
Lithopone, Specification for—Paint. Gov. Pub. 660
Lithopone. Tariff Information Surveys. Gov. Pub. 659
Lixiviator: Potash from Kelp. IV—Continuous Countercurrent Lixiviation of Charred Kelp 605
London Chemical Society's "Annual Reports" at a Reduced Rate. 1007
LONDON LETTER. S. Miall 94, 365, 576, 740, 851, 1084
Longworth Bill: Will the Senate Act? Editorial 2
  The Race Is not Always to the Swift. Editorial 109

MACHINERY, Industrial, in France and Belgium (with Bibliography). Wood. Gov. Pub. 177
MacMichael Viscosimeter in Testing Petroleum Products. Herschel and Dean. Gov. Pub. 370
Magnesite in 1919, 450; in 1920. Yale and Stone. Gov. Pub. 854
Magnesium in 1920. Stone. Gov. Pub. 1088
Maize, Occurrence of Quercetin in Emerson's Brown-Husked Type of. Sando and Bartlett. Gov. Pub. 1175
Maleic and Fumaric Acids, Applications of—and Their Salts in Textile Industry. J. H. Carpenter 410
Maleic and Malic Acids, Production of Coumarins from. G. C. Bailey and F. Boettner 905
MANGANESE:
  In Commonly Grown Legumes. J. S. Jones and D. E. Bullis 524
  Government Publications:
    Deposits near Bromide, Oklahoma. Hewett 964
    Iron and—Ores, Analyzed, Methods of Analysis 743
    Ore, Deposits of—in Batesville District, Arkansas, by Miser, 175; in Montana, Utah, Oregon and Washington, by Pardee 1087
    Ores in 1919. Jenison 580
Mannose, Preparation of—from Ivory-Nut Shavings. P. M. Horton .. 1040
Marble Resources of Southeastern Alaska. Burchard. Gov. Pub. 175
MARKET REPORT .. 103, 183, 279, 375, 499, 587, 667, 747, 859, 971, 1095, 1179
Massachusetts Institute of Technology, School of Chemical Engineering Practice of. R. T. Haslam 465
Measures and Weights. Gov. Pub. 492
Measures and Weights, Specifications and Tolerances for—and Weighing and Measuring Devices. Gov. Pub. 492
Meats Substitute for Sucrose in Curing. Hoagland. Gov. Pub. 272
MEDALS:
  Grasselli Award. Note 1158
  John Scott Award. Note 167
  Medal Awarded to F. B. Power. Note 573
  National Institute of Social Sciences Award. Note 530
  Nichols Award. Announcement, 167; Presentation 567
  Perkin Award, 1921, Announcement, 91; Presentation, ... 158
  1922, Announcement 1126
  Rumford Award. Note 167
Medicinal Products. Tariff Information Surveys. Gov. Pub. 659
Medicinal Products, Chemistry, Division of. Report, New York Meeting, A. C. S. E. H. Volwiler 958
Mellon Institute, Industrial Fellowships of 478
Mercuric Chloride Solution, Reduction in Strength of—Used for Disinfecting Sweet Potatoes. Weimer. Gov. Pub. 965
Metallographic Testing. Gov. Pub. 1089
Metallurgical Works, Accidents at—, U. S., 1919. Adams. Gov. Pub. 491
METALS:
  Government Publications:
    Nonmetals and—, except Fuels. Contributions to Economic Geology, 1919, I. Ransome and Burchard 176
    Other Materials and—, Tests of, Watertown Arsenal, Mass., 1918 97
    Rare. Tariff Information Surveys. Gov. Pub. 659
    Secondary, in 1919. Dunlop 370
    Structure and Related Properties of 1089
Methane Indicators, Permissible—for Mines. Gov. Pub. 491

- Methanol, Improved Denigès Test for Detection and Determination of—in Presence of Ethyl Alcohol. R. M. Chapin 543
- Metric Units, Standard, Adoption by Colleges of. E. C. Bingham 1068
- Mica in 1919. Insley. Gov. Pub 491
- Microanalytical Methods in Oil Analysis. A. H. Gill and H. S. Simms. 547
- Microstructure, Effect of Chemical Reagents on—of Wood. A. Abrams. (*Correction*, 960) 786
- Mildewproofing and Waterproofing of Cotton Duck. Holman, *et al.* Gov. Pub 854
- MILK:
  - Cryoscopy of. J. Hortvet 198
  - Pasteurized, Precipitation of Grain-Curd Casein from—, Including Sweet Cream Buttermilk. H. F. Zoller 510
  - *Government Publications:*
    - Alcohol Test for Determining Quality of—for Condenseries. Dahlberg and Garner 660
    - Dried Milk Preparations and—, Growth Promoting Properties of. Johnson 1087
    - Influence of Calcium and Phosphorus in Feed on—Yield. Meigs and Woodward 661
    - Plant Equipment. Kelly and Clement 97
    - Reconstructed, Studies of. Stevenson, *et al* 175
    - Skim, Antineuritic Vitamine in—Powder. Johnson and Hooper... 1087
    - Sporogenes Test as an Index of Contamination of. Ayers and Clemmer 581
- MINERAL:
  - *Government Publications:*
    - Industries, Industrial Readjustments of 175
    - Lands 369
    - Resources, Fort Hall Indian Reservation, Idaho. Mansfield and Heroy 369
    - Resources of Alaska. Investigations in 1919. Brooks, *et al* 964
    - Resources of U. S. 1917. Part I. Metals, by McCaskey, 490; 1918, by Bastin and Clark, 964; 1920, by Loughlin and Clark 743
    - Supplies, International Readjustment of. Bliss 271
- MINES
  - *Government Publications:*
    - Anaconda Copper Mining Company in Montana, Six-Year Accident Record of. Harrington 854
    - Carbon Monoxide Detector in. Harrington and Dyer 370
    - Lamps, Miners' Flame Safety, in Gaseous, Coal-Dust Laden Atmospheres. Ilsley and Hooker 272
    - Metal, Accidents in U. S., 1919. Adams 580
    - Metal, Compressed-Air Blowers in. Harrington 660
    - Metal, Emergency Fans for Fighting—Fires. Pickard 581
    - Metal, Fire Hazards in. Pickard 272
    - Metal, Hazard in Reopening Long-Flooded Timbered. Harrington. 854
    - Metal, Physiological Effects of High Temperatures and Humidities in. Sayers and Harrington 580
    - Metal, Ventilation in. Preliminary Report. Harrington 491
    - Miner's Safety, Working for. Lyon 491
    - Mining Statutes, Pennsylvania, Annotated. Thompson 491
    - Oxygen Breathing Apparatus in—Rescue Operations. Parker 370
    - Rescue and First-Aid Training, Ten Years of. Bain 580
- Modulus of Hardness of Vulcanized Rubber. H. P. Gurney 707
- Mogollon District, New Mexico. Ferguson. Gov. Pub 369
- Moisture, Determination of—in Insulating Oils. C. J. Rodman 1149
- Moisture Tests, Rapid, Electric Oven for. G. L. Spencer 70
- Motor Vehicles, Gasoline Losses Due to Incomplete Combustion in. A. C. Fieldner, A. A. Straub and G. W. Jones 51
- Moulton, Lord, Death of. Editorial 284
- Mucilage, Cellulose. J. E. Minor 131
- Municipal Wastes. Crohurst. Gov. Pub 175
- Mustard Seeds and Substitutes: I, Chinese Colza. Viehoever, *et al.* Gov. Pub 98

- NATIONAL Academy of Sciences. Gov. Pub 742
  - Memoirs. V—Recalculation of Atomic Weights with Bibliography. Clark. Gov. Pub 742
- National Advisory Committee for Aeronautics. Gov. Pub 97, 175
- NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES. (*See* Exposition)
- NATIONAL FERTILIZER ASSOCIATION:
  - 28th Annual Convention, White Sulphur Springs, W. Va., June 20, 1921. Note 535
  - Chemical Control Committee. Note 738
- National Institute of Social Sciences Medal, Dr. Chandler Receives. 530
- NATIONAL LIME ASSOCIATION:
  - Annual Convention, New York City, June 15 to 17, 1921, 572; Report 653
- NATIONAL RESEARCH COUNCIL:
  - Committee on Chemistry of Colloids. Colloid Development. Report. H. N. Holmes 357
  - Division of Chemistry and Chemical Technology. Report 571
  - Dr. Henry A. Bumstead. Note 167
  - Notes 545, 609
  - Standardization of Biological Stains 1158
- Naval Stores. Tariff Information Surveys. Gov. Pub 742
- Navy Department. Gov. Pub 97
- Neoarsphenamine, Effect of Shaking—in Air. Roth. Gov. Pub 175
- Neoarsphenamine, Keeping Qualities of—in Ampule. Roth. Gov. Pub 1174
- NEW JOURNALS 102, 278, 498, 586
- NEW PUBLICATIONS 102, 182, 278, 374, 498, 586, 666, 746, 858, 970, 1094, 1178
- Newsprint, Recovering. C. Baskerville and R. Stevenson 213
- NICHOLS MEDAL AWARD:
  - Announcement, 167; Presentation 567
- Nickel. Gov. Pub 743
- Nickel and Cobalt, Determination of—in Cobalt Steels. G. E. F. Lundell and J. I. Hoffman 540
- "Nickel, Black," Plating Solutions. Hogaboom, *et al.* Gov. Pub 581
- Nicotine Sulfate as Ovicide and Larvicide. McIndoo, *et al.* Gov. Pub 660
- Nicotine Sulfate in Dust Carrier against Truck-Crop Insects. Campbell. Gov. Pub 370
- Nitric Acid, Sulfate in. Definition of Limits for Impurities in Chemicals. W. D. Collins 948
- Nitric, Proposed Specification for Sulfuric,—and Hydrochloric Acids, and for Ammonium Hydroxide. Reagent Chemicals, I. W. D. Collins 735
- Nitrocellulose and Its Solutions as Applied to Manufacture of Artificial Leather. W. K. Tucker. (*Correction*, 1082) 623
- Nitrocellulose, Removal of Free Acid from—, with Special Reference to Use of Saline Leaches. S. E. Sheppard 1017
- Nitrogen:
  - Atmospheric, for Fertilizers. Davis. Gov. Pub 272
  - Congressional Committee Hearings. Gov. Pub 369
  - Modification of Dumas Method, and Application of Kjeldahl Method to Determination of—in Nitronaphthalenes. P. H. M.-P. Brinton, F. M. Schertz, W. G. Crockett and P. P. Merkel... 636
  - Supply of the World. A. B. Lamb 1166
- Nitrogenous Compounds, Organic, Studies on Availability of—, I. Charles S. Robinson, O. B. Winter and E. J. Miller 933
- Nitroglycerin Spent Acid, Use of—as Charging Acid for Nitric Acid Stills. S. G. Norton 677
- Nitronaphthalenes, Modification of Dumas Method and Application of Kjeldahl Method to Determination of Nitrogen in. P. H. M.-P. Brinton, F. M. Schertz, W. G. Crockett and P. P. Merkel 636
- Nitrotoluenes, Studies on: [*See* THIS JOURNAL, **11** (1919), 1025, 1028, 1124, 1128]
  - V—Binary Systems of *o*-Nitrotoluene and Another Nitrotoluene. J. M. Bell, E. B. Cordon, F. H. Spry and W. White 59
  - VI—Three-Component System: *o*-Nitrotoluene, *p*-Nitrotoluene, 1,2,4-Dinitrotoluene. J. M. Bell and E. B. Cordon 307
  - VII—Three-Component System: *p*-Nitrotoluene, *o*-Nitrotoluene, 1,2,4,6-Trinitrotoluene. J. M. Bell and F. H. Spry 308
- Nodule Bacteria of Leguminous Plants. Löhnis and Hansen. Gov. Pub 370
- NOTES AND CORRESPONDENCE 91, 167, 265, 358, 478, 573, 655, 848, 1079, 1163

- OBITUARIES 489, 1085
- OILS:
  - *Original Papers:*
    - Cold Test Apparatus for. G. H. P. Lichthardt 145
    - Crude, Electrical Dehydration of. W. G. and H. C. Eddy 1016
    - Crude, Viscosity-Temperature Curves of Fractions of Typical American. E. W. Dean and F. W. Lane 779
    - Fats and—, Test for Annatto in. W. Brinsmaid 216
    - Grape-Seed Oil. F. Rabak 919
    - Hollyhock Seed and Oil, Composition of. R. S. Hiltner and L. Feldstein 635
    - Insulating, Determination of Moisture in. C. J. Rodman 1149
    - Iodine Numbers of Unsaturated Hydrocarbons and Cracked Gasolines. W. F. Faragher, F. H. Garner and W. A. Gruse 1044
    - Linseed and Soy-Bean, Effect of Variation in Analytical Constants of—upon Quantitative Determination of Linseed Oil in Mixtures by Means of Iodine and Hexabromide Numbers of Fatty Acids. E. A. Tschudy 941
    - Linseed Oil, Study on Oil Bromide Test of. T. A. Davidson .. 801, 849
    - Microanalytical Methods in Oil Analysis. A. H. Gill and H. S. Simms 547
    - Oil-Field Emulsions, Emulsifying Agents in. J. L. Sherrick 1010
    - Oil-Field Practice in Handling Crude Oil Emulsion. S. Born 1013
    - Oil Shales, Thermal Decomposition of: R. H. McKee and E. E. Lyder.
      - I—Heat Effects 613
      - II—Determination of Heat of Reaction Involved in Thermal Decomposition 678
    - Oil-Water Emulsions, Factors Affecting Stability and Inversion of. L. W. Parsons and O. G. Wilson, Jr 1116
    - Petroleum, Catalytic Oxidation of. C. E. Waters 901
    - Petroleum, Common Characteristics of Crude—Emulsions. E. E. Ayres, Jr 1011
    - Petroleum, Recovering—from Emulsions by Chemical Treatment. R. R. Matthews and P. A. Crosby 1015
    - Rate of Evaporation of Ethyl Chloride from. C. Baskerville and M. Hirsh 322
    - Refractive Indices of. H. S. Simms 546
    - Soy-Bean Oil, Direct Identification of. R. D. Bonney, W. F. Whitescarver and C. A. Newhall. [*See* THIS JOURNAL, **12** (1920), 1174] 574
    - Soy-Bean Oil: Factors Which Influence Its Production and Composition. C. R. Fellers 689
    - Wormwood Oil, Yield and Composition of—from Plants at Various Stages of Growth during Successive Seasons. F. Rabak 536
  - *Government Publications:*
    - Chaulmoogra Oil, Fractionation of. Dean and Wrenshall... 490, 743
    - Chemicals, Paints and—, Reclassification of 659
    - Cottonseed Oil, Survey of American Industry 271
    - Crude, from Eastern Producing Fields, U. S. Dean 370
    - Essential and Distilled. Tariff Information Surveys .... 659 Pub ....
    - Fats and—, Animal and Vegetable, Production, Consumption, Imports, Exports, 1919 and 1920 490
    - Fats and—, Animal and Vegetable. Tariff Information Surveys. 659
    - Lubricating, Carbonization of 272
    - Lubricating, Effect of Crystalline Paraffin Wax upon Viscosity of. Dean and Jackson 660
    - Lubricating, Specifications and Method for Testing 369
    - Oil and Gas Field, Lance Creek, Wyoming. Hancock 176
    - Oil and Gas Permits, Regulations Concerning 175
    - Oil and Gas Resources and Structure of Osage Reservation. Goldman and Robinson 176
    - Oil-Camp Sanitation. Bowie 1089
    - Oil Field, Cement, Caddo County, Okla., Geology of. Reeves 1087
    - Oil Fields, Underground Conditions in. Ambrose 491
    - Oil Possibilities around Baxter Basin, Wyoming. Schultz 369
    - Oil Properties, Relation of Drilling Campaign to Income from. Cutler and Clute 1089
    - Oil-Shale Camps, Sanitation in Planning and Developing. Murray 965
    - Oil-Shale, Notes on—Industry with Particular Reference to Rocky Mountain District. Gavin, *et al* 854
    - Oil Shales, Retort for Assaying—for Oil Yield. Karrick 492
    - Oil Wells, Principles Governing Production of. Beal and Lewis... 660
    - Peanut Oil. Thompson and Bailey 177
    - Peanut Oil, Survey of American Industry 271
    - Petroleum, Sulfur in. Waters 97
    - Physical Crude, from Rocky Mountain District. Dean, *et al* 660
    - Shale Oil, from Bureau of Mines Assay Retort. Gavin and Karrick 854
    - Slushing. Walker and Steele 177
    - Soy-Bean Oil, Survey of American Industry 271
- Olives, Canned Ripe, Bacteriological Study of. Koser. Gov. Pub 177
- Opium. Gov. Pub., 369; Tariff Information, Surveys 659

Oppau Explosion. Editorial Note.......... 975
Ores, Idaho, Flotation Tests of. Wright, *et al.* Gov. Pub.......... 491
Ores, Low-Grade and Complex, in Colorado. Hornor and Coghill. Gov. Pub.......... 370
Ores, Simple Method for Determination of Vanadium in—and Metallurgical Products. R. B. Schaal.......... 698
Organic Chemical Industry:
  Chemistry and the State. F. P. Garvan.......... 866
  Editorial Note.......... 975
  Effective Help. Editorial.......... 751
  President Takes a Hand. Editorial.......... 752
  Resolutions. New York Meeting, A. C. S.......... 873
  Special Cost Factors and Their Relation to Development of Our—. G. Du Bois.......... 1159
Organic Chemistry, Division of. Report, New York Meeting, A. C. S. H. T. Clarke.......... 958
Organic Matter and Organic Carbon, Soil, Rapid Dry Combustion Method for Simultaneous Determination of. J. W. Read.......... 305
Organic Nitrogenous Compounds, Studies of Availability of. Part I. Charles S. Robinson, O. B. Winter and E. J. Miller.......... 933
ORIGINAL PAPERS..59, 110, 198, 292, 406, 504, 600, 672, 757, 893, 1017, 1116
Orthophosphoric Acid, Revised Specific Gravity Table for—at 25°/25° C. N. P. Knowlton and H. C. Mounce.......... 1157
Oven, Electric, for Rapid Moisture Tests. G. L. Spencer.......... 70
Oxalate-Permanganate Titrations, Note on Effect of Presence of Filter Paper on. S. G. Simpson.......... 1152
Oxidation, Catalytic, of Petroleum Oils. C. E. Waters.......... 901
Oxides of Nitrogen, Formation of—in Slow Combustion and Explosion Methods in Gas Analysis. G. W. Jones and W. L. Parker.......... 1154
Oxygen Breathing Apparatus in Mine Rescue Operations. Parker. Gov. Pub.......... 370
Oxygen, Permeation of—Breathing Apparatus by Gases and Vapors. Fieldner, *et al.* Gov. Pub.......... 660
β-Oxynaphthoic Acid, Anilides of. E. R. Brunskill.......... 309
β-Oxynaphthoic Acid, Dyes Derived from—and from J-Acid, with Reference to Chemical Foundation Patents. A. W. Joyce.......... 946
Oyster, Hypochlorite Process of—Purification. Carmelia. Gov. Pub.......... 580

PAINT, Flat Interior Lithopone, Specification for. Gov. Pub.......... 660
Paints. Tariff Information Surveys. Gov. Pub.......... 659
Paints, Chemicals and Oils, Suggested Reclassification of. Gov. Pub... 659
Paints, Semipaste, Specification for Composite Thinner for. Gov. Pub.......... 97
PAPER:
  Apparatus for Rapid Determination of Available Chlorine in Bleach Liquor. M. Schrero.......... 559
  Method for Differentiating and Estimating Unbleached Sulfite and Sulfate Pulps in. Loften and Merritt. Gov. Pub.......... 581
  Recovering Newsprint. C. Baskerville and R. Stevenson.......... 213
  Regenerating Bookstock. C. Baskerville and C. M. Joyce.......... 214
  Testing of. Gov. Pub.......... 660
Paper Trade and Technical Association Conventions.......... 484
"Parazol," Toxic Action of, II. Voegtlin, *et al.* Gov. Pub.......... 175
PARIS LETTER. C. Lormand.......... 94, 171, 269, 366, 576, 657, 852, 962, 1083, 1172
Pastes, Starch and Dextrin, Consistency of. W H. Herschel and C. Bergquist.......... 703
Patent Office. Echoes from the 66th Congress. Editorial.......... 282
Patent Office, Our Anomalous. K. P. McElroy.......... 469
Patents, Assignment of. (*See* Merchant, 849).......... 646
Peanut Oil. Thompson and Bailey. Gov. Pub.......... 177
Peanut Oil Industry, American, Survey of. Gov. Pub.......... 271
Peat in 1920. Cottrell. Gov. Pub.......... 1088
Pennock, J. D. Obituary. E. L. Pierce.......... 489
Perchloric Acid, Use of—as Aid to Digestion in Kjeldahl Nitrogen Determination B. Mears and R. E. Hussey.......... 1054
PERKIN MEDAL AWARD:
  Announcement, 1921.......... 91
  Willis R. Whitney. A. D. Little.......... 158
  Presentation Address. C. F. Chandler.......... 160
  Acceptance Address: Biggest Things in Chemistry. W. R. Whitney.......... 161
  Announcement, 1922.......... 1126
Permanganate-Oxalate Titrations, Note on Effect of Presence of Filter Paper on. S. G. Simpson.......... 1152
Permanganate, Potassium, Note on Use of—in Determination of Nitrogen by Kjeldahl Method. C. T. Dowell, W. G. Friedemann and D C. Cochrane. [*See* THIS JOURNAL, **12** (1920), 1195].......... 358
Permanganates, Sodium and Potassium, Electrolytic Production of—from Ferromanganese. R. E. Wilson, W. G. Horsch and M. A. Youtz. (*Correction*, 960).......... 763
PERSONAL NOTES..95, 173, 270, 368, 488, 578, 658, 741, 853, 963, 1085, 1173
PETROLEUM:
  Petroleum Chemistry, Section of. Report, New York Meeting, A. C. S. W. A. Gruse.......... 959
  Original Papers:
    Action of Anhydrous Stannic Chloride on—and Its Distillates. G. Torossian.......... 903
    Determination of Chlorides in. R. R. Matthews.......... 325
  Government Publications:
    Bibliography of—and Allied Substances in 1918. Burroughs..... 491
    Federal Trade Commission Report on—Industry of Wyoming..... 490
    Geology and—Resources of Northwestern Kern County, California. English.......... 659
    In Alaska, Preliminary Report. Martin.......... 580
    Laws of All America. Thompson.......... 1089
    Naval—Reserves.......... 964
    Pacific Coast—Industry. I.......... 659
    Petroleum.......... 369
    Production in South America with Relation to Recent Petroleum Legislation. Thompson.......... 660
    Products, MacMichael Viscosimeter in Testing. Herschel and Dean.......... 370
    Products, Volatile, Hazards of Handling and Transporting. Bowie.......... 272
    Recent Articles on—and Allied Substances. Burroughs.......... 272, 370, 491, 492, 581, 660, 854, 965, 1089
    Report of Committee on Standardization of—Specifications....... 581
    Tariff Information Surveys.......... 742
Pharmacopeia, U. S. IX, Comments on—and National Formulary (4th ed.). 1917, 175; 1918. DuMez. Gov. Pub.......... 1174
Phenol and Salicylates, Estimation. Studies in Synthetic Drug Analysis, VIII. W. O. Emery.......... 538
Phenols, Detection of—in Water R. D. Scott. (*See* Donaldson, 848, Trowbridge, 848) (*Correction*, 574).......... 422
Phenylglycine-*o*-Carboxylic Acid, Fusion of—for Production of Indigo. Alkali Fusions, III. M. Phillips.......... 759
Philadelphia College of Pharmacy Celebrates One Hundredth Anniversary.......... 354
Philadelphia College of Pharmacy, Centennial of. Note.......... 539
Phosgene, Solvents for. C. Baskerville and P. W. Cohen.......... 333
Phosphate Rock in 1919, 490; in 1920. Stone. Gov. Pub.......... 1087
Phosphate Rock near Maxville, Granite County, Montana. Pardee. Gov. Pub.......... 369
Phosphates, Acid Calcium, Determination of "Strength" or Neutralizing Power of. W. E. Wadman.......... 1146
Phosphoric Acid, Investigation of U. S. P. Assay for—and Soluble Phosphates. A. E. Stearn, H. V. Farr and N. P. Knowlton.......... 220
Phosphorus:
  Government Publications:
    In Fertilizer. Waggaman.......... 1174
    Influence of Calcium and—in Feed on Milk Yield. Meigs and Woodward.......... 661
    Leaching Iron Ores for. Winslow.......... 965
Photography. A Special Problem. Editorial.......... 188
Photography, Industrial and Technical. Note.......... 1060
Phthalic Anhydride Derivatives, Names and References. M. Phillips. (*See* Linz, 363).......... 247
Phthalic Anhydride, Pure. J. Bebie. [*See* THIS JOURNAL, **12** (1920), 1017, Andrews, **13** (1921), 167].......... 91
Physical and Inorganic Chemistry, Division of. Report, New York Meeting, A. C. S. S. E. Sheppard.......... 956
Phytase, Activity of—as Determined by Specific Conductivity of Phytin-Phytase Solutions. F. A. Collatz and C. H. Bailey.......... 317
Pickles, Fermented. Le Fevre. Gov. Pub.......... 272
Picric Acid as a Blasting Agent. Munroe and Howell. Gov. Pub..... 581
Pine-Oil and Pine-Distillate Product Emulsions. Shippen and Griffin. Gov. Pub.......... 1174
Pipe, Concrete, Flow of Water in. Scobey. Gov. Pub.......... 492
Pipe, Concrete, Use of—in Irrigation. Stanley. Gov. Pub.......... 492
Plants, Influence of Cold on Growth of. Coville. Gov. Pub.......... 98
Plaster, Colored Wall. Emley and Faxon. Gov. Pub.......... 492
Plating: "Black Nickel" Plating Solutions. Hogaboom, *et al.* Gov. Pub.......... 581
Plating: Zinc Cyanide Plating Solutions. Blum, *et al.* Gov. Pub..... 1089
Platinum:
  Allied Metals and—in 1920. Hill. Gov. Pub.......... 1088
  Editorial Note.......... 5
  In Ores, Detection and Estimation of. Davis. Gov. Pub.......... 491
  Metals, Estimation of—in Material High in Copper. Davis. Gov. Pub.......... 491
  Production. Note.......... 695
  Thefts. Notes..........316, 697
Poland, Restoration in. Editorial.......... 671
Polysulfides, Theory of Accelerators Based on Formation of—during Vulcanization. Reactions of Accelerators during Vulcanization, II. W. Scott and C. W. Bedford.......... 125
Porcelain Glazes, High Fire. Sortwell. Gov. Pub.......... 1089
Potash:
  Alsatian—Industry.......... 227
  American—Industry and Its Problems. J. E. Teeple. Address..... 249
  Centrifugal Method for Determining. E. Sherrill. (*Correction*, 480).......... 227
  From Kelp. (*See* Kelp)
  In 1919, by Hicks and Nourse, 176; 1920, by Nourse. Gov. Pub.... 1174
  Resources of Nebraska. Hicks. Gov. Pub.......... 369
  Shales of Illinois. M. M. Austin with S. W. Parr.......... 1146
  Tariff Information Surveys. Gov. Pub.......... 659
Potassium:
  Chlorate, New Crystalline Form of. E. R. Walcott.......... 215
  Compounds, Application of Vapor Pressures of—to Recovery of Potash by Volatilization. D. D. Jackson and J. J. Morgan.......... 292
  Compounds, Measurement of Vapor Pressures of. D. D. Jackson and J. J. Morgan.......... 110
  Concentration of—in Orthoclase Solutions not Measure of Availability to Wheat Seedlings. Breaseale and Briggs. Gov. Pub.... 370
  Hydroxide Alcoholic, Preparation of—Volumetric Solution. S. T. McCallum.......... 943
  New Method for Determination of—in Silicates. J. J. Morgan..... 225
  Permanganate, Note on Use of—in Determination of Nitrogen by Kjeldahl Method. C. T. Dowell, W. G. Friedemann and D. C. Cochrane. [*See* THIS JOURNAL, **12** (1920), 1195].......... 358
Potatoes:
  Absorption of Copper from Soil by Potato Plants. Cook. Gov. Pub.......... 1175
  Composition of Tubers, Skins, and Sprouts. Cook. Gov. Pub..... 370
  Freezing Injury to. Wright and Taylor. Gov. Pub.......... 743
  Potato Flour and Mineral Constituents of: Effect of Process of Manufacture on Composition of the Ash of Potato Flour. C. E. Mangels.......... 418
  Sweet, Canned, Discoloration in. E. F. Kohman.......... 634
  Sweet, Reduction in Strength of Mercuric Chloride Solution Used for Disinfecting. Weimer. Gov. Pub.......... 965
Poultry Feed Mixtures, Potential Acidity and Alkalinity of. Kaupp and Ivey. Gov. Pub.......... 98
Power, F. B., Presentation of Medal to.......... 573
Preservatives, Cider. R. D. Scott and E. G. Will.......... 1141
Preservatives: Toxicity of Various Fractions and Combinations of Fractions of Coal-Tar Creosote to Wood-Destroying Fungi. H. Schmitz and S. M. Zeller.......... 62
Preservatives, Wood, Studies on Toxicity of. III. C. J. Humphrey, R. M. Fleming and E. Bateman.......... 618
President of United States. Gov. Pub.......... 964
Priestley, Presentation of—Portrait. C. A. Browne. Address, New York Meeting, A. C. S.......... 879
Printing Strike:
  An Acknowledgment. Editorial.......... 750
  Fair Weather Predictions. Editorial.......... 590
Problems of National Defense. J. W. Wadsworth, Jr. Address, Rochester Meeting, A. C. S.......... 382
Professors, Exchange, in Engineering and Applied Science between French and American Universities. Note.......... 574
Public Health Service: Evolution and Organization. Gov. Pub....... 659
  Government Publications.......... 97, 175, 271, 490, 580, 659, 743, 964, 1087, 1174

Publications for Sale by Superintendent of Documents: Agricultural Chemistry, Industrial Alcohol, Preservatives. Gov. Pub 175
Pulps, Soda and Sulfate, Chemical Constitution of—from Coniferous Woods and Their Bleaching Qualities. S. D. Wells 936
Pulps, Unbleached Sulfite and Sulfate, Method for Differentiating and Estimating—in Paper. Lofton and Merritt. Gov. Pub 581
Pyroxylin Plastics. Tariff Information Surveys. Gov. Pub 659

QUARRY Accidents in U. S., 1919. Adams. Gov. Pub 491
Quartz Media, Non-Biological Oxidation of Elementary Sulfur in. W. H. MacIntire, F. J. Gray and W. M. Shaw 310
Quercetin, Occurrence of—in Emerson's Brown-Husked Type of Maize. Sando and Bartlett. Gov. Pub 1175
Quicksilver in 1919. Ransome. Gov. Pub 580

RADIATION Effects in Thermometry. Clark S. Robinson 820
Raffinose, Revision of Optical Method for Analyzing Mixtures of Sucrose and. C. A. Browne and C. A. Gamble 793
Ramsay, Sir William, Memorial of. Note 363
Rats, Toxicity of Barium Carbonate to. Schwartze. Gov. Pub 98
Reagent Chemicals. I—Proposed Specification for Sulfuric, Nitric, and Hydrochloric Acids, and for Ammonium Hydroxide. (Suppl. A.C. S. Committee Report) W. D. Collins 735
Reagents, Unit Weights for Purchase of,—II. [*See* THIS JOURNAL, **12** (1920), 1206] W. D. Collins 473
Receiver for Vacuum Fractionations. P. Gross and A. H. Wright 702
Receivers, Telephone, for Electrometric Work. C. C. Kiplinger 713
RECENT JOURNAL ARTICLES 102, 182, 278, 374, 498, 586, 666, 746, 858, 970, 1094, 1178
Refining Raw Sugars without Bone-Black. C. E. Coates 147
Refractometer, Immersion, Application of—to Analysis of Aqueous Salt Solutions. C. A. Clemens 813
Refrigerator Machines, Ammonia Absorption, Noncondensable Gases in. McKelvy and Isaacs. Gov. Pub 272
Repairing Iron Leaching Vats. Note. C. Flury 168
Research. E. F. Smith. Address, Joint Meeting, New York Chemical Societies 254
Research and Standardization. S. W. Stratton. Address 727
Research Chemicals, Manufacture of—at University of Wisconsin. 323
Research, Industrial, Plan for Development of—in Canada. R. F. Ruttan. Address, New York Meeting, A. C. S 876
RESEARCH PROBLEMS IN COLLOID CHEMISTRY. W. D. Bancroft 83, 153, 260, 346
Ringstand Set. C. D. Carpenter 332
Rocks, Igneous, Geology of—, Essex County, Mass. Clapp. Gov. Pub 490
Rubber:
  Action of Certain Organic Accelerators in Vulcanization of. [*See* THIS JOURNAL, **12** (1920), 317] G. D. Kratz, A. H. Flower and B. J. Shapiro. II, 67; III 128
  Crude, Variability of. J. B. Tuttle. (*See* Stevens, 1165) 519
  Energy. W. B. Wiegand 118
  Gutta-Percha and. Tariff Information Surveys. Gov. Pub 743
  Hydrocarbon, Discussion of Tetrabromide Method for Estimating. H. L. Fisher, H. Gray and R. Merling 1031
  Influence of Certain Organic Accelerators on Vulcanization of. G. S. Whitby and O. J. Walker 816
  Reactions of Accelerators during Vulcanization. [*See* THIS JOURNAL, **12** (1920), 31]
    II—Theory of Accelerators Based on Formation of Polysulfides during Vulcanization. W. Scott and C. W. Bedford 125
    III—Carbo-Sulfhydryl Accelerators and the Action of Zinc Oxide. C. W. Bedford and L. B. Sebrell 1034
  Recent Development in Art of—Microsectioning. H. Green 1130
  Rubber Chemistry, Division of. Report, New York Meeting, A. C. S. A. H. Smith 957
  Testing of—Goods. Gov. Pub 1089
  Volume Increase of Compounded—under Strain. H. Green. [*See* THIS JOURNAL, **12** (1920), 33] 1029
  Vulcanized, Modulus of Hardness of. H. P. Gurney 707
  Vulcanized, Relation between Coefficient of Vulcanized and Mechanical Properties of. O. de Vries 1133
RUMFORD MEDAL. Note 167

SACCHAROMYCETES, Action of Ultraviolet Rays on. R. De Fazi, B. Feuer and F. W. Tanner. [*See* THIS JOURNAL, **12** (1920), 740] 265
Safety and Health. Allen and Murray. Gov. Pub 660
Safety and Health, Miners', Almanac 1921. Williams. Gov. Pub 177
Safety Lamps, Miners' Flame, in Gaseous, Coal-Dust Laden Atmospheres. Ilsley and Hooker. Gov. Pub 272
Safety Lamps, Miner's Flame, Permissible, Procedure for Establishing List of. Gov. Pub 491
Safety, National—Code for Protection of Heads and Eyes of Industrial Workers. Gov. Pub 492
Salicylates and Phenol, Estimation of. Studies in Synthetic Drug Analysis, VIII. W. O. Emery 538
Salt, Aqueous, Application of Immersion Refractometer to Analysis of—Solutions. C. A. Clemens 813
Salt, Bromine and Calcium Chloride in 1920. Stone. Gov. Pub 965
Salt in 1919. Insley. Gov. Pub 490
Salt, Permian, Deposits of South-Central U. S. Darton. Gov. Pub 580
Sampling, Continuous, of Sugar Liquors. W. L. Jordan 640
Sand and Gravel in 1919. Stone. Gov. Pub 271
Sanitation: Death Erroneously Attributed to Chlorinated Water. Emerson. Gov. Pub 1174
Sanitation: Detection of Phenols in Water. R. D. Scott. (*See* Donaldson, 848; Trowbridge, 848) (*Correction*, 574) 422
Sanitation: Role of Acidity in Dehydration of Sewage Sludge. J. A. Wilson and H. M. Heisig 406
Sanitation: Typhoid Fever Epidemic, Greenville, Tenn. Harrub. Gov. Pub 271
Sardine Industry, Maine. Weber, *et al*. Gov. Pub 272
Sawdust, Hydrolyzed, Preparation and Analysis of Cattle Food Consisting of. E. C. Sherrard and G. W. Blanco 61
Scales, Large Capacity, Precision Test of. Briggs and Gordon. Gov. Pub 1089
Schedules, Permissible, Issued by Bureau of Mines. Ilsley. Gov. Pub 491
SCIENTIFIC SOCIETIES 89, 166, 266, 352, 480, 567, 651, 733, 844, 951, 1068, 1168
SCOTT, JOHN, MEDAL AWARD. Note 167
Seal, Graded, for Joining Pyrex to Lead Glass. W. C. Taylor and A. Bailey 1158
Searles Lake Brine, Alkalinity of. R. C. Wells 691
Selenium in 1920. Heickes. Gov. Pub 1088
Sewage, Sanitary Disposal of—through Septic Tank. Crohurst. Gov. Pub 175, 490
Sewage Sludge, Role of Acidity in Dehydration of. J. A. Wilson and H. M. Heisig 406
Sewage Testing Station of Illinois State Water Survey Division. E. Bartow 945
Shale Oil, Commercial—Production. Sharp. Gov. Pub 491
Shale Oil from Assay Retort, Bureau of Mines. Gavin and Karrick. Gov. Pub 854
Shale, Oil-, Notes on—Industry with Particular Reference to Rocky Mountain District. Gavin, *et al*. Gov. Pub 854
Shales, Oil, Thermal Decomposition of: R. H. McKee and E. E. Lyder.
  I—Heat Effects 613
  II—Determination of Heat of Reaction Involved in Their Thermal Decomposition 678
Shales, Potash, of Illinois. M. M. Austin with S. W. Parr 1144
Shortening: Its Definition and Measurement. C. E. Davis 797
Silage, Bacteriological and Chemical Studies. Hunter. Gov. Pub 1174
Silica in 1919. Beach. Gov. Pub 1087
Silicates: Application of Vapor Pressures of Potassium Compounds to Recovery of Potash by Volatilization. D. D. Jackson and J. J. Morgan 292
Silicates, New Method for Determination of Potassium in. J. J. Morgan 225
Silver:
  Government Publications:
    Divide Silver District, Nevada. Knopf 369
    Estimation of—in Material High in Copper. Davis 491
    Production (1919) Eastern States, by Dunlop, 175; Alaska, by Brooks and Martin; California and Oregon, by Yale, 580; Central States, by Dunlop, 659; Arizona and Utah, by Heikes, 965; Idaho, by Gerry; Nevada, by Heikes; Montana, by Gerry, 1087; South Dakota and Wyoming, by Henderson 1174
      (1920) Eastern States, by Dunlop 1087
    Vitamine Compound. Seidell 490
Sink, Laboratory. C. D. Carpenter 332
Skin Irritant, Mercury Fulminate as. III. Livingston. Gov. Pub 175
Slate as Permanent Roofing Material. Bowles. Gov. Pub 965
Slate in 1919. Loughlin and Coons. Gov. Pub 1087
Smith, E. F. Society's President for 1921. F. P. Venable 106
Smithsonian Institution. Gov. Pub 175, 271
Smokes, Combustion. G. A. Richter 343
Soap, Rapid Method for Determination of Sodium Chloride in. H. C. Bennett 813
Soaps. Tariff Information Surveys. Gov. Pub 659
Soapstone in 1919. Diller. Gov. Pub 580
SOCIAL INDUSTRIAL RELATIONS. H. W. Jordan 473
  Biological Trend of Industry 650
  Crowds and Their Manners 566
  Editorial Note 405
  Food and Shelter 1161
  Method for Social Research 1066
  Out-of-Door Education for the Chemist 731
  Science of Human Engineering 844
  Social Research 949
  Spare Time. (*See* Editorial "Your Brother's Keeper," 187; Sprague, 474; Joyce, 651; and Dedlow, 1067) 253
SOCIÉTÉ DE CHIMIE INDUSTRIELLE:
  Annual Meeting, Paris, France, October 9 to 12, 1921. Note 904
  Chemical Exposition, October 7 to 16, 1921. Note 904
SOCIETY OF CHEMICAL INDUSTRY:
  Annual General Meeting, Montreal, Canada, August 29 to 31, 1921:
    Program 732, 845, 863
    Report 862
Sodium:
  Chloride, Rapid Method for Determination of—in Soap. H. C. Bennett 813
  Compounds, by Wells, in 1919, 176; in 1920, 1089; Tariff Information Survey. Gov. Pub 659
  Hydroxide, Solid, as Absorbent for Carbon Dioxide in Steel Analysis. G. L. Kelley and E. W. Evers 1052
  Oxalate as Standard in Volumetric Analysis. Gov. Pub 97
Soils:
  Original Papers:
    Measuring Soil Toxicity, Acidity, and Basicity. R. H. Carr 931
    Methods for Determining Amount of Colloidal Material in. C. J. Moore, W. H. Fry and H. E. Middleton 527
    Non-Biological Oxidation of Elementary Sulfur in Quartz Media. W. H. MacIntire, F. J. Gray and W. M. Shaw 310
    Rapid Dry Combustion Method for Simultaneous Determination of Soil Organic Matter and Organic Carbon. J. W. Read 305
  Government Publications:
    Effect of Season and Crop Growth on Physical State of. Hoagland and Martin 177
    Relation of Calcium Content of Kansas Soils to Reaction Determined by Electrometric Titration. Swanson, *et al* 492
    Silty Clay Loam, Effect of Crops upon Water Extract of. Stewart and Martin 370
    Temperature to Which—Can Be Cooled without Freezing. Bouyoucos 370
Soy-Bean Oil:
  Direct Identification of. R. D. Bonney, W. F. Whitescarver and C. A. Newhall. [*See* THIS JOURNAL, **12** (1920), 1174] 574
  Factors Which Influence Its Production and Composition. C. R. Fellers 689
  Linseed and—, Effect of Variation in Analytical Constants of—upon Quantitative Determination of Linseed Oil in Mixtures by Means of Iodine and Hexabromide Numbers of Fatty Acids. E. A. Tschudy 941
  Survey of American—Industry. Gov. Pub 271
Spain, Import and Export Schedules of. Gov. Pub 177
Spare Time. H. W. Jordan. (*See* Editorial "Your Brother's Keeper," 187; Sprague, 474; Joyce, 651, and Dedlow, 1067) 253
Specific Gravity Table, Revised, for Orthophosphoric Acid at 25°/25°C. N. P. Knowlton and H. C. Mounce 1157
Spencer Electric Oven, Dry Substance in Molasses, Sirups and Juices by. G. P. Meade 924
Stains, Biological, Standardization of 1158

- Standardization and Research. S. W. Stratton. Address 727
- Standardization, Report on—of Sizes and Shapes of Apparatus, I. W. D. Collins 1070
- Stannic Chloride, Anhydrous, Action of—on Petroleum and Its Distillates. G. Torossian 903
- Starch. Tariff Information Surveys. Gov. Pub 742
- Starch, Consistency of—and Dextrin Pastes. W. H. Herschel and C. Bergquist 703
- Steel:
  - Analysis, Solid Sodium Hydroxide as Absorbent for Carbon Dioxide in. G. L. Kelley and E. W. Evers 1053
  - Centrifugally Cast, Test of. Gov. Pub 742
- Steels, Annealed Carbon, Relation between Brinell Hardness and Grain Size of. Rawdon and Jimeno-Gil. Gov. Pub 97
- Steels, Cobalt, Determination of Cobalt and Nickel in. G. E. F. Lundell and J. I. Hoffman 540
- Stenches for Detecting Leakage of Blue Water Gas and Natural Gas. Katz and Allison. Gov. Pub 177
- Still, Combined Extractor, Reflux Condenser,—and Autoclave. A. T. Shohl and M. L. Koch 819
- Stills, Nitric Acid, Use of Nitroglycerin Spent Acid as Charging Acid for. S. G. Norton 677
- Storage, Changes in Florida Grapefruit in. Hawkins and Magness. Gov. Pub 177
- Storage, Common, Relation of Moisture Content to Deterioration of Raw-Dried Vegetables upon. H. C. Gore and C. E. Mangels 523
- Strontium in 1919, 176; in 1920. Stose. Gov. Pub 1089
- SUGARS:
  - Sugar Chemistry, Division of. Report, New York Meeting, A. C. S. F. J. Bates 957
  - *Original Papers:*
    - Cane Juice, Effect of Some Decolorizing Carbons upon Color and Colloids of. J. F. Brewster and W. G. Raines, Jr 921
    - Cane Juice, Effect of Varying Hydrogen-Ion Concentration upon Decolorization of—with Carbon. J. F. Brewster and W. G. Raines, Jr 1043
    - Cane Juices, Lead-Preserved, Determination of Reducing Sugars in. J. B. Harris 925
    - Crystals, Examination of—by Projection. G. P. Meade 712
    - Desugarization, Comparison of Results in—with Steffen Lime, Barium, and Strontium Processes. M. Potvliet 1041
    - Digester, Rotary, for Use in Bagasse Analysis. G. L. Spencer 640
    - Electric Oven for Rapid Moisture Tests. G. L. Spencer 70
    - Mannose, Preparation of—from Ivory-Nut Shavings. P. M. Horton 1040
    - Molasses, Sirups and Juices, Dry Substance in—by Spencer Electric Oven. G. P. Meade 924
    - Rare, Standardization of. H. T. Graber 687
    - Rare: Their Purity and Tests. C. Pfanstiehl and R. S. Black 685
    - Refining Raw Sugars without Bone-Black. C. E. Coates 147
    - Sampling, Continuous, of Liquors. W. L. Jordan 640
    - Sucrose and Raffinose, Revision of Optical Method for Analyzing Mixtures of. C. A. Browne and C. A. Gamble 793
    - Sucrose, New Qualitative Test for—in Presence of Glucose. L. A. Congdon and C. R. Stewart 1143
    - Sugar Beets, Process for Producing Palatable Sirup from. S. F. Sherwood 799
  - *Government Publications:*
    - Coöperative Cane-Sirup Canning. Dale 98
    - Deterioration in Storage. Kopeloff, *et al* 370
    - Galactose, Preparation of. Clark 1089
    - Sucrose, Substitute for—in Curing Meats. Hoagland 272
- Sulfate, Ammonium, Effect of—upon Plants in Nutrient Solutions Supplied with Ferric Phosphate and Ferrous Sulfate. Jones and Shive. Gov. Pub 1174
- Sulfate in Nitric Acid. Definition of Limits for Impurities in Chemicals. W. D. Collins 948
- Sulfates, Relation of—to Plant Growth and Composition. Miller. Gov. Pub 1175
- Sulfur:
  - Distribution of Forms of—in Coal Bed. H. F. Yancey and T. Fraser 35
  - Elementary, Non-Biological Oxidation of—in Quartz Media. W. H. MacIntire, F. J. Gray and W. M. Shaw 310
  - Factors Affecting—Content of Coke and Gas in Carbonization of Coal. A. R. Powell 33
  - Forms, Analysis of—in Coal. Powell. Gov. Pub 660
  - In Petroleum Oils. Waters. Gov. Pub 97
  - Pyrites and. Tariff Information Surveys. Gov. Pub 964
- Sulfuric Acid Solutions, Humidity Control by Means of—, with Critical Compilation of Vapor Pressure Data. R. E. Wilson 326
- Sulfuric, Proposed Specification for—, Nitric, and Hydrochloric Acids, and for Ammonium Hydroxide. Reagent Chemicals, I. W. D. Collins 735
- SWITZERLAND, CHEMICAL INDUSTRY AND TRADE OF. O. P. Hopkins 285
- Synthetic Organic Chemical Manufacturers Association of U. S.:
  - Meeting, New York City, September 15, 1921 891
  - Organization. Note 1168

TALC:

  - High-Grade—and California Industry. Ladoo. Gov. Pub 660
  - In 1919. Diller. Gov. Pub 580
  - Industry in 1920. Ladoo. Gov. Pub 370
  - New—Grinding Capacity in U. S. Ladoo. Gov. Pub 580
- Tannin Content of Pacific Coast Conifers. R. H. Clark and H. I. Andrews 1026
- Tannin, Determination of. J. A. Wilson and E. J. Kern 772
- Tanning Materials. Tariff Information Surveys. Gov. Pub 659
- Tanks, Lease, Prevention of Evaporation Losses in. Wiggins. Gov. Pub 660
- Tar, Dehydration of—in the Laboratory. W. J. Huff 1123
- Tariff Bill:
  - Congressional Recognition of Chemistry. Editorial 592
  - Effective Help. Editorial 751
  - Have You Done Your Share? Editorial 670
  - President Takes a Hand. Editorial 752
- Tariff Bill, Emergency. A Tragedy Averted. Editorial 502
  - Editorial Note 975
- Tariff, Chemical Industry from a—Viewpoint. C. R. DeLong 470
- Tariff Commission. Gov. Pub 175, 369, 659, 742, 964
- Tariff Information Surveys. Gov. Pub 659, 742, 964
- TECHNICAL ASSOCIATION OF PULP AND PAPER INDUSTRY:
  - Annual Meeting, New York City, April 11 to 14, 1921. Announcement 331
  - Joint Meeting with American Pulp and Paper Mill Superintendents' Association, Washington, D. C., October 18 to 21, 1921. Announcement 943
  - Cancellation of Joint Meeting. Note 1007
- Tellurium, Health Hazard in Industry. Shie and Deeds. Gov. Pub 175
- Tellurium in 1920. Heickes. Gov. Pub 1088
- Tetrabromide Method, Discussion of—for Estimating Rubber Hydrocarbon. H. L. Fisher, H. Gray and R. Merling 1031
- Textiles: Applications of Maleic and Fumaric Acids and Their Salts in Textile Industry 410
- Thermal Decomposition of Oil Shales. (*See* Shales, Oil)
- Thermal Expansion of Copper and Its Alloys. Hidnert. Gov. Pub 743
- Thermometers, Laboratory. W. D. Collins 240
- Thermometers, Partial and Total Immersion, Note on. C. W. Waidner and E. F. Mueller 237
- Thermometers, Testing of. Gov. Pub 1089
- Thermometry, Radiation Effects in. C. S. Robinson 820
- Thinner, Composite, Specification for Semipaste Paints. Gov. Pub 97
- Thymol, and Carvacrol (Isothymol), Comparative Toxicity of. Livingston. Gov. Pub 743, 1174
- Tin Salts. Tariff Information Surveys. Gov. Pub 659
- Titration Bench. W. A. VanWinkle 146
- Titration, Electrometric, Determination of Chromium in Ferrochromium by. G. L. Kelley and J. A. Wiley 1053
- Titration, Electrometric, Determination of Vanadium and Chromium in Ferrovanadium by. G. J Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright 939
- Tomato, Waste Seed from Pulping Industry. Shrader and Rabak. Gov. Pub 581
- Toxicity, Comparative, of Thymol and Carvacrol (Isothymol). Livingston. Gov. Pub 743, 1174
- Trent Process, Laboratory Studies of. G. St. J. Perrott, *et al.* Gov. Pub 965
- Tricalcium Arsenate, Preparation and Instability of. J. H. Reedy and I. L. Haag 1038
- Trinitrotoluene Poisoning—I. Voegtlin, *et al.* Gov. Pub 175
- Tungsten Deposits, Contact-Metamorphic, of U. S. Hess and Larsen. Gov. Pub 1087
- Tungsten in 1918. Hess. Gov. Pub 490
- Tungsten Mine, Minerals from—, Trumbull, Conn. Shannon. Gov. Pub 175
- Turpentine, Detection and Estimation of Coal-Tar Oils in. V. E. Grotlisch and W. C. Smith 791
- Turpentine, Standard Specifications for. Gov. Pub 743
- Typhoid Fever Epidemic, Greenville, Tenn. Harrub. Gov. Pub 271

- **U**LTRAVIOLET Rays, Action of—on Saccharomycetes. R. De Fazi, B. Feuer and F. W. Tanner. [*See* THIS JOURNAL, **12** (1920), 740] 265
- United Waist League Conference, New York City, September 13, 1921. 982
- Urea, Determination of Dicyanodiamide and of—in Fertilizers. E. Johnson 533

- **V**ACUUM Drying. C. O. Lavett and D. J. VanMarle 600
- Vanadium and Chromium, Determination of—in Ferrovanadium by Electrometric Titration. G. L. Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright 939
- Vanadium, Simple Method for Determination of—in Ores and Metallurgical Products. R. B. Schaal 698
- Vanilla Extracts, New Lead Number Determination in. H. J. Wichmann 414
- Vapor Composition of Alcohol-Water Mixtures. P. N. Evans and W. K. Lewis. [*See* Lewis, THIS JOURNAL, **12** (1920), 296] 168
- Vapor Pressure, Apparatus for Demonstrating—of Liquids. C. D. Carpenter 332
- Vapor Pressures, Measurement of—of Certain Potassium Compounds. D. D. Jackson and J. J. Morgan 110
- Varnish, Asphalt, Specification for. Gov. Pub 97
- Varnish, Spar, Specification for. Gov. Pub 97
- Varnishes. Tariff Information Surveys. Gov. Pub 659, 742
- Vats, Iron Leaching, Repairing. C. Flury. Note 168
- Vegetables, Dehydrated, Effect of Heat on. C. E. Mangels and H. C. Gore 525
- Vegetables, Raw-Dried, Relation of Moisture Content to Deterioration of—upon Common Storage. H. C. Gore and C. E. Mangels 523
- Vegetation, Motor Fuel from. T. A. Boyd 836
- Ventilation: Compressed Air Operated—Doors in Arizona Copper Mines. Gardner. Gov. Pub 1089
- Vibration Absorbers. Comparative Study of. H. C. Howard 231
- Vinegar, Labeling of. Note 930
- Viscosimeter, Saybolt Furol. Dean. Gov. Pub 491
- Viscosity-Temperature Curves of Fractions of Typical American Crude Oils. E. W. Dean and F. W. Lane 779
- Vitamines: (*See* also A.C. S. New York Meeting, Symposium)
  - Antineuritic, in Skim Milk Powder. Johnson and Hooper. Gov. Pub 1087
  - Chemistry of. A. Seidell 72
  - Silver—Compound. Seidell. Gov. Pub 490, 743
- Volatile Matter, Determination of—in Graphite. O. L. Shinn 633
- Voorhees, Samuel Stockton. Obituary. W. F. Hillebrand 1085
- Vulcanization, Action of Certain Organic Accelerators in—of Rubber. [*See* THIS JOURNAL, **12** (1920), 317] G. D. Kratz, A. H. Flower and B. J. Shapiro. II, 67; III 128
- Vulcanization, Influence of Certain Organic Accelerators on—of Rubber. G. S. Whitby and O. J. Walker 816
- Vulcanization, Reactions of Accelerators during:
  - II—Theory of Accelerators Based on Formation of Polysulfides during Vulcanization. W. Scott and C. W. Bedford 125
  - III—Carbo-Sulfhydryl Accelerators and Action of Zinc Oxide. C. W. Bedford and L. B. Sebrell 1034
- Vulcanization, Relation between Coefficient of—and Mechanical Properties of Vulcanized Rubber. O. de Vries 1133

- **W**AR DEPARTMENT. Gov. Pub 97, 175, 369, 964
- War Making, Modern. Developments in. W. J. Pope. Address, New York Meeting, A. C. S. 874
- Warfare, Modern, Incendiaries in. A. B. Ray 641, 71
- WASHINGTON LETTER 92, 169, 268, 364, 486, 575, 656, 739, 850, 961, 1082, 1171
- Wastes, Industrial, Disposal of. Hommon. Gov. Pub 490
- Wastes, Municipal. Crohurst. Gov. Pub 175
- WATER:
  - Water, Sewage and Sanitation, Division of. Report, New York Meeting, A. C. S. W. W. Skinner 959

Organic Fluids:
  Alcohol-Water Mixtures, Vapor Composition of. P. N. Evans and W. K. Buskirk. (See This Journal, 12 (1920), 296) ... 165
  Calcium Chloride Method for Determination of—in Gasoline and in Certain Other Substances. C. W. Clifford ... 628
  Detection of Minute ... in. R. D. Scott. (See Donaldson, 848; Thompson, 848; Correction, 974) ... 422
  Heater for Analytical Work. S. L. Meyers ... 362
  Softening for Manufacture of Raw Water Ice. A. S. Behrman ... 235
  Solubility of—in Gasoline and in Certain Other Organic Liquids, Determined by Calcium Chloride Method. C. W. Clifford ... 631
Government Publications:
  Amount of—that Seeds Cause to Become Unfree. Bouyoucos and McCool ... 370
  Chlorinated, Death Erroneously Attributed to. Emerson ... 1174
  Ground, Exploratory Drilling for—and Use of—for Irrigation, Steptoe Valley, Nev. Clark et al. ... 271
  Ground, for Irrigation, Gage, Ellis County, Okla. Thompson ... 1087
  Ground, in Connecticut: Meriden Area, by Waring, 580; Norwalk, Suffield and Glastonbury Areas, by Palmer, 271; Southington Granby Area, by Palmer ... 580
  Levels, Records of—in Southern California. Ebert ... 580
  Mineral Waters in 1919. Ellis ... 370
  Supply of St. Mary and Milk Rivers, 1898–1917. Jones and Barnes ... 492
  Supply, Selection and Protection of Sources of. Hoskins ... 580, 964
  Surface—Supply of Pacific Slope, Southern California. McGlashan ... 580
  Surface—Supply of U. S. Grover et al.
    1917. Part III—Ohio River Basin ... 175
    1917. Part VI—Missouri River Basin ... 492
    1917. Part IX—Colorado River Basin; Part X—The Great Basin ... 1088
    1917. Part XII—Northern Pacific Slope Drainage Basins. (A) Pacific Basins in Washington and Upper Columbia River Basin ... 580
    1918. Part I—North Atlantic Slope Drainage Basins ... 964
    1918. Part V—Hudson Bay and Upper Mississippi River Basins; Part VI—Missouri River Basin ... 1087
    1918. Part XI—Pacific Slope Basins in California ... 659
  Watering Places, Routes to—in Mohave Desert Region, Cal. Thompson ... 964
Water Gas Apparatus and Use of Central District Coal as Generator Fuel. Odell. Gov. Pub ... 660
Waterproofing and Mildewproofing of Cotton Duck. Holman et al. Gov. Pub ... 584
Waterproofing: Water Resistance of Treated Canvas during Continuous Exposure to Weather. F. P. Veitch and T. D. Jarrell ... 672
WATTS, SIR FRANCIS, IMPERIAL COMMISSIONER OF AGRICULTURE: INDUSTRIAL AND AGRICULTURAL CHEMISTRY IN BRITISH WEST INDIES, WITH SOME ACCOUNT OF WORK OF. C. A. Browne ... 78
Wax, Crystalline Paraffin, Effect of—upon Viscosity of Lubricating Oil. Dean and Jackson. Gov. Pub ... 661
Waxes, Vegetable and Mineral. Tariff Information Surveys ... 742
Weight Variation of Package Goods. Runkel. Gov. Pub ... 97
Weights and Measures. Gov. Pub ... 492
Weights and Measures, Specifications and Tolerances for—and Weighing and Measuring Devices. Gov. Pub ... 492
Wheat. Gov. Pub.:
  Changes Taking Place in Tempering of. Tague ... 370
  Relation of Hardness and Other Factors to Protein Content. Roberts ... 965
  Seed, Injury to—after Disinfection with Formaldehyde ... 272
  Seedlings, Concentration of Potassium in Orthoclase Solutions not Measure of Availability to. Breazeale and Briggs ... 370
Wisconsin, Manufacture of Research Chemicals at University of. 323
Women, Employment of—in Hazardous Industries in U. S. Gov. Pub ... 97
Wood:
  Coniferous Woods, Chemical Constitution of Soda and Sulfate Pulps from—and Their Bleaching Qualities. S. D. Wells ... 936
  Effect of Chemical Reagents on Microstructure of. A. Abrams. (Correction, 967) ... 786
  Estimation of Cellulose in. B. Johnsen, W. H. Dore and S. A. Mahood. (See This Journal, 12 (1920), 264, 873) ... 318
  Experimental Study of Significance of "Lignin" Color Reactions. E. C. Crocker ... 625
  Studies on Toxicity of Wood Preservatives, III. C. J. Humphrey, R. M. Fleming and E. Bateman ... 618
  Toxicity of Various Fractions and Combinations of Fractions of Coal-Tar Creosote to Wood-Destroying Fungi. H. Schmitz and S. M. Zeller ... 621
  Wood Chemical Industry. Tariff Information Surveys. Gov. Pub ... 659
Wormwood Oil, Yield and Composition of—from Plants at Various Stages of Growth during Successive Seasons. F. Rabak ... 316

YEAST: Action of Ultraviolet Rays on Saccharomycetes. R. De Fazi, B. Feuer and F. W. Tanner. (See This Journal, 12 (1920), 743) ... 265
Yeast, Brewers', Silver Vitamine Compound from. Seidell. Gov. Pub ... 743

ZINC:
  Cyanide Plating Solutions. Blum et al. Gov. Pub ... 1088
  Determination of Small Quantities of. M. Bodansky ... 696
  In 1918. Siebenthal. Gov. Pub ... 580
  Oxide, Carbo-Sulfhydryl Accelerators and Action of. Reactions of Accelerators during Vulcanization, III. C. W. Bedford and L. B. Sebrell ... 1034
  Production (1919). Gov. Pub. Eastern States, by Dunlop, 175; California and Oregon, by Yale, 580; Central States, by Dunlop, 659; Arizona and Utah, by Heikes, 965; Idaho, by Gerry; Nevada, by Heikes; Montana, by Gerry ... 1087
    (1920) Eastern States, by Dunlop ... 1087
  Sulfate, Electrical Conductivity of Solutions of—in Presence of Sulfuric Acid. H. V. Tartar and H. E. Keyes ... 1127
Zirconium, Metal and Oxide. Historical Review and Bibliography. Marden and Rich. Gov. Pub ... 1089

BINDING LIST NOV 1 1954

TP
1
I13
v.13
pt.2

I&EC. Industrial and
engineering chemistry

~~Physical &~~
~~Applied Sci.~~

ENGINEERING
Engineering

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY

ENGIN STORAGE